

SECONDARY BATTERIES

THEIR THEORY, CONSTRUCTION AND USE.

BY

E. J. WADE, M.I.E.E.

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AUTHOR'S NOTE.

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IN the five years that have elapsed since this book first appeared the lead storage battery has well maintained its position as a very desirable and, in many cases, almost indispensable adjunct to lighting and power plants, little affected apparently by the contention of those who think it should be displaced in favour of more generators ; consequently the increase in its employment has been quite commensurate with the general growth of the electrical industry.

During this period there have been no additions of importance to the theory of the cell's action, and few alterations have been made in the details of its design and construction, except such as were necessary to bring the various commercial types more thoroughly into accordance with what was already recognised as the best practice in 1903, the ultimate result being that the cells of the leading manufacturers now present a very great similarity as regards their main features all the world over. Thus the Electrical Power Storage Co. now provide formed positives for nearly all their stationary types, the D.P. Battery Co, chiefly employ large

Author's Note.

surface cast positives with the usual deep horizontal ribs closely spaced, and the Chloride Electrical Storage Co. has given up the use of negative active material prepared from lead chloride.

In several instances the design of the negative supports has been modified so as to increase the area of contact with the active material at the surfaces of the plate, with a view to a better maintenance of capacity. Thus the Tudor Co., the Chloride Co., and the D.P. Co. all now employ a grid with rather large apertures, but having both faces covered with finely perforated lead. The grid is made in two halves, which are joined together, back to back, after the active material has been filled into them, thus forming a kind of cage for it.

Practically all the makers now suspend the electrodes of stationary cells by lugs well above the level of the electrolyte, and resting upon the edges either of the containing box or of vertical glass slabs; and they leave a very ample space between the lower edges of the electrodes and the floor of the box. A few introduce sheets of some kind of porous insulating material between the plates. For this purpose the Chloride Co. use diaphragms of specially prepared porous wood. The Hart Accumulator Co. employ nitrated cellulose fibre mounted on a web of similar spun fibre.

Apart from the alterations just mentioned, the matter of Chapter X. is not now in strict accord with its title, "Present Day Cells," in one other respect, inasmuch as some of the cells there described, mostly designed for use in automobiles, and of minor importance, are no longer present, having failed to justify their existence, but the

Author's Note.

ingenuity embodied in their construction still gives them considerable interest. Other types have not arisen to take their place, for the evolution of the light-weight traction cell has lately made very little progress, the tendency at present being rather in favour of heavier but more durable cells, with electrodes on the lines of those used in the stationary types, especially for the heavier classes of electrical vehicles, such as motor 'buses and lorries.

In 1903 there was some reason to believe that the problem of producing a commercial accumulator with an alkaline electrolyte was on the verge of solution, but, in spite of the undoubtedly promising results furnished by cells which Edison sent to Europe in that year for laboratory tests, the commercial article is not yet forthcoming. In the absence of any authoritative statement as to the reasons of this prolonged delay, we can only conclude that the "great and unforeseen difficulties experienced in connection with the positive plate," mentioned in one of Edison's later patent specifications, are largely responsible. It appears from the context that the difficulties in question are the insufficient conductivity of the nickel oxide or other material constituting the positive active material. The publications of the Patent Office bear eloquent testimony to the strenuous efforts that are being made to overcome all obstacles, but it is yet too early to attempt to say what will be the outcome of the struggle.

E. J. WADE,

PREFACE.

THE title of this volume implies one dealing with a whole class of apparatus. Such is indeed the scope; nevertheless, it substantially resolves itself into a treatise on the lead/lead peroxide combination—the storage cell of commerce—because all others still seem to be practically negligible. In this very fact lies the interest of the subject from some points of view. With copper as the commercial conductor of electricity and iron as the only practical magnetic metal, we are content, feeling that we would not have chosen otherwise, and that in any case we are confronted with something fundamental which cannot be altered; but to lead, with its weight and its weakness (and all the limitations which these entail), as the sole agent for the storage of electrical energy on any considerable scale we cannot finally resign ourselves.

The matter must eventually be settled in one of two ways. Either different and better means will be found, or else it will be demonstrated that lead also holds its

place in virtue of certain inherent properties which, like conductivity and permeability, are of the nature of things in themselves. Meanwhile, as time goes on, it seems more and more probable that the lead cell, although standing alone, is truly typical of certain conditions which any successful storage cell will have to possess, and that progress may best be encompassed by a more careful study of the known instance. In this connection it may be noted that the latest and most promising attempt at a new departure—*i.e.*, Edison's Cell, with its active materials of porous iron and nickel oxide in an electrolyte in which they are *both* insoluble under all ordinary conditions of use—embodies a partial compliance with the chief characteristic of the lead cell, as the Author predicted in 1900 that any practical combination would have to do. Whether it also complies with the remainder by having both active materials of reasonable conductivity is more doubtful, and it is this which probably delays its commercial introduction and may prove fatal to its ultimate success.

The preceding considerations should more than justify the devotion of a good many of the following pages to the theory of the lead cell and the details of the physical and chemical changes through which it achieves its results. Even should their ultimate explanation involve a *non possumus*, so far as other feasible storage cells are concerned, it would be strange indeed if the labour were wasted or failed to indicate some direction in which the lead cell might itself be improved and the sphere of its usefulness augmented.

In electro-chemical problems the dissociation hypothesis is supposed to furnish the key to all mysteries,

but in the present instance it affords little help where help is really needed ; while other points, such as those relating to the varying concentration of the electrolyte, can be better and more simply discussed without its aid. In the Author's opinion, some of the earlier and what are now considered old-fashioned ways of dealing with electrolytic actions are here of much more use, and he has in the main adhered to them, and especially to the quite unjustly discredited thermo-chemical point of view.

Turning to more practical matters, it will be found that the major portion of the book treats the accumulator purely from the point of view of an appliance—a machine, in fact, but with all its motions of molecular dimensions only—which fulfils an important and definite purpose in electrical engineering practice, and whose manufacture, use and properties must be understood just as much as those of a generator or a transformer.

Some indulgence must be asked for Chapter VI., on the design of lead cells. This subject has been largely ignored by most writers on accumulators, and with good reason, for directly an attempt is made to deal with it one encounters a number of closely related variables, but finds that precise information as to how any individual one of them varies is entirely lacking. Until this deficiency is remedied by what would certainly be a prolonged and perhaps somewhat tedious investigation, cell designing must largely remain a matter of the eye and of instinctive knowledge derived from experience. Meanwhile, it seemed wiser and more useful merely to discuss the general nature of and relationship between the different variables rather than to express one's ignorance in algebraical equations and empirical formulæ.

All the particulars of modern cells given in Chapter X. have been compiled either from information directly furnished by the makers, or from published statements. Naturally, different views are held as to how far it is expedient to make known the details of manufacture, design and performance, and to this must be ascribed the scantiness of the description in some cases compared with its fulness in others.

In conclusion, the Author desires to express his thanks for the large amount of assistance that has been so freely rendered him in making this chapter as complete as possible.

E. J. WADE.

London, November, 1902.

CONTENTS.

CHAPTER I.

	PAGE
INTRODUCTORY	1
Early History—Planté's Researches—Further Developments— Relationship of Primary and Secondary Cells—Nomenclature— Components of Electrodes—Classification of Electrodes.	

CHAPTER II.

HISTORICAL—LEAD CELLS	14
Material of Supports—Active Material—Grid Supports— Double Grids—Recessed and Pocket Supports—Studded Sup- ports—Tube, Trough and Bar Electrodes—Moulded Pellet Elec- trodes—Protected Electrodes—Plate and Sheet Protection— Tubular and Rod Electrodes—Thin Sheet and Strip Supports— Wire Supports—Metallic Envelope Electrodes—Volckmar or "Plugged" Electrodes—Planté or "Formed" Electrodes— Grooved or Ribbed Supports—Thin Sheet Electrodes—Crimped or Pleated Sheet Electrodes—Strip Electrodes—Vertical Strip Electrodes—Coiled Strip Electrodes—Porous Electrodes— Arrangement of Electrodes—Series Batteries.	

CHAPTER III.

STORAGE CELLS OTHER THAN LEAD	115
The Thomson-Houston Cell—Sutton's Cell—Reynier's Copper/ Lead Peroxide Cells—Zinc/Sulphuric Acid/Lead Peroxide Cells— Reynier's Zinc/Lead Peroxide Cells—Main's Cells—Epstein's Zinc Cells—Output of Zinc/Lead Peroxide Cells—Defects of Zinc/Lead Peroxide Cells—The Lalande-Chaperon Cell—Des- mazes' Cells—The Waddell-Entz Cell—Alkaline Cells with Other Negatives—Output of Zinc/Copper Oxide Cells—Defects of Zinc/Copper Oxide Cells—Edison's Alkaline Cells.	

CHAPTER IV.

THE PROPERTIES AND BEHAVIOUR OF LEAD CELLS 145

Discharge Reactions—E.M.F. of Discharge—Curves of Discharge P.D.—Reactions on Charge—Polarisation E.M.F.s of Recharge—Curves of Recharge P.D.—Capacity and Output—Influence of Method of Recharge upon Output—Influence of Temperature upon Output—Efficiency—Efficiency of Traction Batteries—Internal Resistance.

CHAPTER V.

THE CHEMISTRY OF LEAD CELLS 203

Historical—The Oxidation Theory of Discharge—Mixture versus Combination—Polymerisation Theory of the Cell's Action—Thermo-Chemistry of the Cell—Temperature Changes during Discharge and Recharge.

CHAPTER VI.

THE DESIGN OF LEAD CELLS..... 253

Active Materials—Supports—Electrodes—Output for Weight of Electrode—Relative Output of Positives and Negatives—Design of Electrodes—Electrolyte—Tables of Specific Gravity of Sulphuric Acid Solutions at 15°C.—Position of Electrodes—Separating—Supporting—Automobile Cells.

CHAPTER VII.

THE MANUFACTURE OF LEAD CELLS 291

Active Material—Planté Formation—Quick Formation Processes—Pasted Active Material—Formation—Lead Chloride as Raw Active Material—Electrolyte.

CHAPTER VIII.

THE TREATMENT AND TESTING OF LEAD CELLS 325

Treatment on Discharge—Treatment on Recharge—Treatment on Open Circuit—Treatment of Sulphated Cells—Treatment of Short-Circuited Cells—Commercial Testing—Laboratory Testing—Chemical Testing—Iron—Copper—Manganese—Arsenic—Nitric and Nitrous Acids—Hydrochloric Acid.

CONTENTS.

ix.

PAGE

CHAPTER IX.

THE ERECTION, CONNECTING-UP AND REGULATION OF LEAD CELLS	357
--	-----

Arrangement—Stands for Cells—Insulators for Cells—Connectors—First Charging—Hydrometers—Cell-Testing Voltmeters—Automatic Cut-in-and-Out Switches—Connecting-up—Regulating—Reserve Cells—Counter E.M.F. Cells—Booster Regulation—Automatic Regulation.

CHAPTER X.

PRESENT DAY CELLS	395
-------------------------	-----

"E.P.S."—"Crompton-Howell"—"D.P."—"Epstein"—English "Chloride"—"Tudor"—"P. and G."—"Hart"—"A. B. P."—"P. T. L."—"Leitner"—"Lithanode"—"Monobloc"—"Allan"—"Armoured"—"Marquand"—"Gulcher" or "Woven Glass"—"Pollak"—"Sherrin" or "Pope"—"Still" or "Ideal"—"Rosenthal" or "National"—"Taipo"—"Oppermann"—"Umpire." American Cells: American "Chloride"—"Gould"—"Willard"—"American"—"Porter"—"Clare"—"Reuter-dahl"—"Sperry"—"Osburn"—"Conrad." Continental Cells: "Tudor" and "A. F. A."—"Hagen" or "K. A. W."—"Pollak"—"Khotinsky" or "Bleistaub"—"Lehmann"—"Boese"—"Behrend"—"Schulz"—"Watt"—"Tribelhorn"—French "Chloride" or "T. E. M."—"Blot"—"Blot Fulmen"—"D'Arsonval-Vaugeois"—"Fulmen"—"B. G. S."—"Heinz"—"Majert" or "Union"—"Phenix"—"Max"—"Cheval-Lindeman"—"De Dion-Bouton." Accumulators other than Lead/Lead Peroxide.

CHAPTER I.

INTRODUCTORY.

Early History.

The reversibility of the primary or ordinary galvanic cell, as exemplified in the secondary or storage cell, is but one more instance of the universal law of action and reaction. Hardly had the voltaic pile been invented before it was discovered that, when at work, it developed some resisting or opposing force which tended to choke down the flow of current; and, further, if it were connected to a pair of metal plates or wires dipping into some saline-conducting liquid, these latter themselves acquired the power of giving a momentary current after disconnection from the pile. Gautherot first observed this phenomenon in 1801, while decomposing salt water with wires of silver or platinum. Two years later Ritter obtained the same effects with gold wires, noticed the formation of metallic films and peroxides by electrolytic action, and embodied the results of his observations in his secondary pile, which consisted of discs of copper separated by pads moistened with saline solutions, and which, when charged by a primary battery composed of a larger number of elements than itself, could give out transitory currents of considerable intensity.

These secondary currents were rightly thought to be due to the recombination of the acids and bases set free when the salts were decomposed by the passage of the primary current. Some years later, however, it was observed that similar currents could be obtained from platinum wires used to decompose dilute sulphuric acid, or even pure water, and as, in this case, the metal was not oxidised nor were there any salts present to be decomposed, it was maintained that they

must have a physical rather than a chemical origin, and the wires were said to be "polarised," while the phenomenon itself was termed "polarisation." During the years that followed, numerous investigators were constantly at work on the subject, but nearly all from the same point of view and with the same object. They regarded polarisation effects as of no value in themselves, but only to be studied in order the better to be able to destroy or reduce them to a minimum, and so increase the efficiency of primary cells; and it was during this period that the Daniell, Grove, Bunsen and other constant current cells were invented.

It was conclusively proved, however, that polarisation was always due to purely chemical causes, and, in the cases just mentioned, was the result of the decomposition of the water itself into its constituent gases, which were liberated at either pole and generated secondary currents during their recombination. Platinum wires, which had been immersed in oxygen and hydrogen gas respectively, gave currents just the same as those which had had a primary current passed through them, and Sir W. Grove constructed his celebrated gas battery, which he described in 1842, on this principle. Although Grove set up his battery by the addition of oxygen and hydrogen previously prepared, he could, as he well knew, have energised it by sending a current through the electrodes and decomposing the water; and it may be considered, therefore, as the earliest form of reversible battery which was fully recognised as such. In fact, no storage cell of more recent date presents the principle on which their action depends in a simpler or more striking form than does this gas cell of Grove's; so that, although practical difficulties stand in the way of its adoption commercially, it will always possess a very considerable theoretical interest.

The line of research, however, that it might naturally be thought to have suggested was not followed up, because in those days the need of a cell for the storage of electricity was not felt, and even if one had been invented it could have been of very little use. Primary cells were then the only known source of dynamic electricity on any practical scale, and to have set up a number of these merely to charge a smaller number of secondary cells, instead of using them direct for

the purpose in view, would obviously only have been a waste both of labour and material.

Planté's Researches.

Gaston Planté was the first to investigate polarisation phenomena with a view to their utilisation instead of their elimination, and in 1859 he commenced the series of researches which are recorded in his well-known work. The experiments he carried out and the apparatus he employed were of the very simplest nature. Rods of various metals were, in turn, placed in a small acid voltameter or electrolytic cell, and a current passed through it from two or three Bunsen cells; then, by means of a simple form of mercury switch, the battery was cut out of the circuit, and the voltameter at once connected to a sensitive galvanometer. In this way he carefully examined the polarisation of all the ordinary metals, and found that, although in some instances very slight and transitory, every one of them gave secondary currents; but that those obtained with lead electrodes in dilute sulphuric acid far exceeded the others, both in duration and intensity. Guided by this observation, he then constructed his famous spiral form of lead accumulator, investigated the best method of "formation" for increasing its capacity, and utilised a number of such cells to carry out a variety of experiments with larger currents than it would have been possible to obtain at that date without their aid. His book* will be found extremely interesting reading, not only on account of its suggestiveness and the information it contains, but also as an example of the results that may be obtained from the minute and accurate observation of the simplest phenomena. Although, owing to the limitations of electro-chemical knowledge at that date, his explanations of some of his experiments were necessarily incorrect, later investigations have never in the smallest particular impugned the accuracy of the experiments themselves, while many of the points to which he drew attention have only been rediscovered in comparatively recent years. He noticed the evolution of oxygen from the peroxide pole on breaking the charging circuit; the formation of peroxide at the spongy

* "The Storage of Electrical Energy," by Gaston Planté. Translated by P. B. Elwell, 1887.

lead pole when discharged; the presence of unstable compounds (hydrogen peroxide and persulphuric acid) in the electrolyte: and he further remarked that these latter were produced in greater abundance with lead than with platinum electrodes.

Further Developments.

Although Planté showed how more or less practical storage cells could be constructed, even yet the time was not ripe for their commercial utilisation and development, and no further advances were made for some years; but, as soon as the evolution of the dynamo reached such a stage as to render the production of large currents at high potentials a comparatively easy and inexpensive matter, interest in the subject revived. In 1881 Camille A. Faure took out his patent for preparing the active material of lead storage cells from oxides or other salts mechanically applied to the surface of the electrodes, thereby obviating Planté's long and wearisome process of formation from the material of the electrodes themselves, and the history of the practical storage of electricity may be said to have commenced from that date. From 1881 to 1885 inventors in England, the United States of America and the Continent of Europe vied with each other in working out and patenting new designs of lead cells based on the methods both of Planté and of Faure, and, in many instances, practically the same idea was recorded almost simultaneously in two or more countries. Since that time no fresh departure in principle has been made, and of all the numberless types of cells that have been brought out, very few embody any features in design, whose prototype cannot be found in the work of those early years. At the same time, the improvements that have been effected in the details of construction and proportion of parts, and in the methods of manufacture and treatment, while small in themselves, yet enable far more satisfactory results to be obtained than was formerly possible.

The interest and avidity with which Faure's cell was received and taken up caused attention to be turned to the construction of accumulators with electrodes of other metals than lead, for it was perceived that these offered far greater possibilities as regards the amount of energy that could be

stored for a given weight of metal. Sutton's copper/lead cell, Reynier's zinc/lead cell, and the Thomson-Houston zinc/copper cell were amongst some of the earliest forms of the different combinations tried, and since then the problem has been again and again attacked, but with such little success that, at the present day, lead/lead peroxide cells hold the entire field, the remainder being regarded as but little more than electrical curiosities.

Relationship of Primary and Secondary Cells.

The sharp distinction thus created between lead accumulators and all other cells, whether primary or secondary, naturally suggests that there must be some fundamental difference in their principles of action; but this is not the case, and the real explanation is to be found in what may almost be termed the *accidental* suitability of the chemical behaviour of lead and certain of its compounds to the purpose to be achieved. Theoretically, there is no difference between a storage or secondary cell and a primary cell; both are apparatus for the conversion of chemical into electrical energy. The use of lead peroxide as a depolariser was known to Faraday and others long before Planté studied it; and if electrolytically-prepared peroxide is packed round a core of lead and put in dilute sulphuric acid with a similar electrode packed with electrolytic lead in a porous or spongy state, the combination forms what would ordinarily be termed a primary cell, but one possessing all the chief characteristics of a lead accumulator. On the other hand, if, instead of putting fresh materials into an exhausted Daniell cell, a current is passed through it in the reverse direction, it forms a Thomson-Houston accumulator; if an exhausted Lelande-Chaperon cell is treated in the same way, it becomes, in principle, the storage cell of Desmazes and many others, and, as has been shown above, the Grove gas cell is either a primary or secondary cell according to the way in which it is set up. In reality, therefore, every secondary cell is also a primary cell, and every primary cell a possible secondary cell. Even a Grove or Bunsen cell might be regenerated electrically if special appliances were provided to collect the gases that escape during the discharge; and

Planté showed that every one of his combinations gave some sign, however slight, of secondary currents.

The whole question resolves itself into one of the degree of practical reversibility. Whether it is possible, by passing a current in the opposite direction, to exactly reverse the changes that took place while discharging, and restore a cell to the same condition, both chemically and physically, that it occupied at first; or whether it is easier to re-energise it by removing the spent materials and substituting others in their place. Here, then, lies the superiority of a lead/lead peroxide cell to all others. If properly treated, it may be regenerated electrically, and so nearly restored to its original chemical and physical state that it can be discharged and charged in this way hundreds or even thousands of times before the culminative effect of the slight changes that do take place depreciates it sufficiently to incapacitate it for further use; while, with all other combinations, the changes that occur with each charging are relatively so large that, although every possible means has been tried to reduce them to a minimum, the cells rapidly deteriorate and require constant repairs and renewal.

Nomenclature.

The three terms "secondary cell," "storage cell," and "accumulator" are used indifferently to describe those galvanic cells which possess sufficient reversibility to be of practical use. In their early days, before they had emerged from the experimental stage and the laboratory, they were almost exclusively known by the first of these three (or else as "polarisation cells"), and it is still occasionally given the preference, being considered more scientifically accurate than the other two more popular cognomens. Its chief characteristic is to emphasise the difference between secondary and primary galvanic cells, and as this distinction is far more arbitrary than true, it does not appear that its claim to any special applicability can be substantiated. It is quite possible that at any time some modification of well-known types of primary cells might largely improve their practical reversibility and render them commercially useful for storage purposes, in which case the term would be more confusing than otherwise.

On the other hand, exception has sometimes been taken to the terms "storage cell" and "accumulator," on the ground that the cells do not really store or accumulate anything; but it is difficult to see what basis there is for this objection. Of course, the popular notion that the cells store electricity as *electricity* is, strictly speaking, quite incorrect; but the change or conversion of the substances of which the electrodes and electrolyte are composed from a lesser to a more highly energised state does constitute a very real storage or accumulation of energy, and quite sufficiently justifies the use of the terms. Further, as it is electricity which brings about these changes, and electricity which again results from their reversal, the cells do in substance, if not in fact, act as storers or accumulators of electricity.

The fact that cells containing lead electrodes are so far the only ones that have proved at all satisfactory commercially has enabled them to largely appropriate the title that by rights belongs to a whole class, so, unless specially qualified, the terms mentioned above are tacitly understood to imply lead cells, and will be used in that sense throughout this book. Probably the term "reversible lead cells," which was used by Mr. D. G. FitzGerald in the title of a Paper read by him in 1884, is the most satisfactory name that could be given to them, but it has never come into any extensive use.

Following primary battery nomenclature, the terms "secondary battery" and "storage battery" are sometimes used with reference to single cells; but, to avoid confusion, the word "battery" should be exclusively reserved to describe the combination of a number of cells, or else in a purely collective sense, as applied to the whole class. To distinguish the actual containing vessel from the cell as a whole, the former is now called the "box" by the manufacturers, and this word is being generally adopted.

Another point of storage battery nomenclature which has given rise to a great deal of confusion is that of the polarity of the electrodes. In primary cells, chiefly from electrostatic considerations, the electrode at which oxidation takes place—generally zinc—is termed the positive, and that at which hydrogen is liberated, or where reduction and depolarisation are effected—usually copper, carbon or platinum—the

negative. The current is assumed to pass from the positive electrode through the electrolyte to the negative electrode, and thence by the external circuit back to the positive again.

The negative electrode, therefore, is the one of highest potential, and that by which the current leaves the cell; and on this account it is called the positive pole, just as the terminal of a dynamo by which the current passes into the external circuit is the positive. That is to say, in a primary cell the positive plate or electrode is the negative pole, and the negative plate or electrode is the positive pole.

In secondary cells this confusing distinction has not been maintained. The terminal by which the current leaves the cell on discharging, and which is connected to the positive of the dynamo on charging, is correctly termed the positive pole, but the name has also been extended to the electrodes themselves, and consequently the peroxide plates are now called the "positives," and the reduced lead plates the "negatives."

Although this use of the names is just the reverse of their original application, yet it has so firmly and universally established itself that it must be conformed to to make oneself intelligible to practical men, and it would only appear pedantic to attempt to do otherwise. It must, however, always be borne in mind that the reduced lead plates, or so-called negatives, are the true positives, corresponding to the zinc or oxidisable electrode of primary cells, and that the peroxide plates are really negatives, corresponding to the carbon or depolarising electrode.

Components of Electrodes.

Every lead accumulator plate, of whatever type, consists fundamentally of two parts, *i.e.*, the "active material" and the "support." The active material is that portion which actually undergoes the chemical changes by means of which electrical energy is alternately given out and absorbed during discharge and charge. It may be prepared in a variety of ways and from numerous materials, but when completed and in its most highly energised state—that is to say, in a fully-charged cell—it always consists of lead peroxide at the positive electrode and lead at the negative electrode. As, however, its activity depends entirely on its reactions with the electrolyte, its

physical structure is of as much importance as its chemical composition, and it is only when in a finely subdivided or porous form that it can exhibit any considerable amount of storage capacity. "Active material" may be practically defined, therefore, as those portions of the electrodes to which the electrolyte has more or less complete molecular access, and it is this property that distinguishes the active material of the negative electrode from its support; for, in this instance, they are chemically of similar composition, *i.e.*, lead. At the positive electrode the difference is one both of composition and of structure. •

It may be mentioned in passing that, when speaking of the various substances and mixtures employed in the manufacture of accumulator plates, and intended to be converted into true active material in the final stages, they are all, for want of a more convenient phrase, sometimes included in the term "active material," although, to be strictly accurate, they should be described as "material to become active," or "raw active material."

The support, variously termed the "frame," "grid," "backing," &c., according to the form it takes, is that portion of the electrode which, as its name implies, holds the active material together in its place, and also acts as a conductor to collect the current from all parts and convey it to the connecting lug or terminal. Occasionally these two functions are divided up between separate portions of the support—the one a conductor, the other a non-conducting material. In some types of electrodes it is attempted to combine the whole of the mechanical, electrical and chemical requirements in the active material itself, and dispense with the support as much as possible, but even here it has to be employed in a rudimentary form to effect a connection with the external circuit.

Classification of Electrodes.

Lead storage cells are usually classified into "Faure" or "pasted" cells and "Planté" or "formed" cells. The first class comprises all those electrodes whose raw active material is applied to the support in the form of spongy lead or of oxides or other salts of lead, either in a moist or dry condition. It also includes those electrodes whose active material, usually in a raw state, is first prepared in pieces of a suitable

size and shape by casting or moulding, and the support afterwards cast round them. The second class consists of electrodes in which the active material is produced from the surface of the support itself by electro-chemical means.

This classification not only serves to indicate the different methods of manufacture associated with the respective names, but it also frequently connotes certain distinctive features in the combining and arranging of the active material and its support resulting from these methods. In most of the *Faure type electrodes* the active material is present in comparatively large undivided masses, held more or less rigidly in position by the surrounding support, while in the *Planté type electrodes* the active material is distributed over the faces of the support in thin layers, the latter being so constituted as to offer a large surface within a small compass for this purpose, and in most instances the two hold together more by virtue of their intimate contact than by reason of any direct pressure exerted between them.

It should be remembered, however, that these special features do not necessarily go with the type to which an electrode belongs, and there are some plates which it would be difficult to classify merely from inspection and without knowing how they were manufactured. Moreover, even if the type of an electrode is clearly marked when new, its distinctive character frequently tends to become obliterated in the course of working. This change is confined to positives, and is brought about by the wasting and replenishment of active material that is constantly going on. For instance, there are many positive electrodes which, although nominally "pasted," yet have a support possessing a large surface area out of which peroxide is formed in the course of working in sufficient quantity to maintain their capacity, even after the whole of the applied active material has fallen out. On the other hand, *Planté positives* may gradually acquire some of the attributes of the pasted types through this same production of peroxide, for the films covering the walls of the support gradually increase in thickness until adjacent layers meet and the whole of the interstices are filled with a porous, but continuous mass of active material, just as though it had been mechanically applied in the first instance.

There are a few electrodes which, broadly speaking, belong to the Planté type, but as they embody a distinct feature in construction they really form a small class by themselves of what may be termed "Volckmar" or "plugged" plates, after E. Volckmar, the first patentee of electrodes of the kind in question. They come intermediate between the two main types, and combine some of the characteristics of each of them. Their speciality consists in the fact that their active material, although electro-chemically formed from metallic lead, is not produced from the substance of the support itself, but from a number of independent pieces of metal, or plugs which are merely gripped and held together by the support proper, just as is the active material of most electrodes of the Faure type. The plugged positives undergo the change of character in working just referred to more readily than any other of the Planté plates, and, in fact, they have in many instances been designed with this object in view. The pieces of metallic packing first become further disintegrated and then entirely peroxidised, so that portions of active material wholly relying for their support on the surrounding frame, and of considerable size, are finally produced.

CHAPTER II.

HISTORICAL.—LEAD CELLS.

In the following chapter a summary is given of the various types of lead cells that have been proposed since the year 1881, and this chiefly resolves itself into an account of the different kinds of electrodes. Many that seem of no use have been omitted, but it does not follow that much or any value attaches to every one described. Very few of them have been a commercial success, the majority only having a brief career in a more or less tentative and experimental stage, while a large number have never passed beyond the laboratory and patent specification. As, however, the fundamental principles of accumulator design still remain to be decided and formulated, and methods of construction that have been abandoned as wrong and old-fashioned are frequently revived a few years afterwards as the very latest improvement, it is evident the time has not yet arrived for pronouncing a very definite judgment on the relative merits of past efforts. Certainly many ideas now almost forgotten are quite as good, and perhaps a little better, than some that by a fortunate turn of circumstances have survived in practice and are more generally known.

An endeavour has been made, therefore, to put on record all proposals that appear to contain a possible germ of utility, and to give the credit for each particular mode of construction to its first originator. Later revivals of the same idea are not necessarily mentioned unless combined with other modifications, and for this reason the work of the last few years does not figure very largely in the list. The electrodes are grouped together according to some common feature in their design or construction, in preference to placing

them in their historical sequence, a plan which would only lead to much bewilderment; but this rough classification is quite empirical and not founded on any strictly scientific basis, for many of the electrodes could equally well be classed in several different ways according to which of their characteristics was selected for the purpose. The arrangement adopted follows the lines indicated at the end of the previous chapter, *i.e.*, Faure type electrodes and Planté type electrodes, each subdivided under a number of headings, and a small intermediate class of Volckmar or "plugged" electrodes.

Material of Supports.

The supports in the electrodes of the original lead cells of both Planté and Faure were of unalloyed lead. J. S. Sellon claimed the use of frames constructed of alloys of lead and antimony in one of his 1881 patents, but the claim, if valid, does not appear to have been upheld, and lead or antimonious lead, or a combination of the two, has been almost universally employed for supports ever since. Many endeavours have been made, however, to introduce other metals, not for the purpose of taking any part in the reactions of the cell, but merely as inert conductors which should distribute the currents to and from the spongy lead and lead peroxide at their respective electrodes. It was hoped in that way to provide a support which should be lighter than lead and less liable to electrochemical corrosion by local action than that metal.

Platinum and gold, either pure or alloyed, were even considered as possible materials for supports, notwithstanding their great cost, but naturally, for this reason, the amount to be employed was always cut down to the very smallest limits. J. S. Sellon proposed the use of thin platinum foil as a backing for a pasted form of electrode in 1881. In the following year C. F. Brush claimed the use of alloys of platinum with lead, and in 1883 D. G. FitzGerald and T. J. Jones proposed the same thing, mentioning 1 to 80 as a suitable proportional composition. Platinum foil was used in the early "Lithanode" or solid peroxide plates, and in 1885 T. J. Jones and W. H. Tasker described various arrangements of foil, held and interwoven in frames of insulating material, for application to this class of electrode, but in all these cases the platinum served

purely for conducting purposes, and, rather than affording any support, was itself supported by the active material in which it was embedded.

In 1883 A. J. Jarman suggested alloys of lead and silver, and in 1885 E. Julien proposed to alloy about 1 per cent. of mercury with antimonious lead, to render it more unoxidisable.

In spite of its poor conductivity, early investigators made frequent attempts to substitute carbon as a material for supports, partly on account of its small weight, and partly with a view to avoiding local action between the support and active material of the positive electrode. Sellon mentioned its use in 1881 in the first accumulator patent he took out, and in the following year J. W. Swan proposed to construct frames or supports of compressed plumbago, while about the same time F. Maxwell Lyte prepared a dense form of carbon for the same purpose from various organic mixtures, treated and baked with sugar, syrup, &c., to consolidate them. J. Swinburne also experimented with carbon supports in 1883.

Another method of utilising carbon was to impregnate some porous variety with a solution of a soluble salt of lead, and then reduce it to a metallic state by heat or electrolysis. Dr. Werner von Siemens had treated it in this way in 1852 to form electrodes for his reversible gas cells. In 1881 Fitzgerald proposed to similarly treat carbon fragments and pack them in perforated cylinders of lead or carbon or some insulating material with a central lead conductor, but in a later patent, while limiting the use of carbon to the negative electrode, he extended the treatment to whole plates. H. Sutton also proposed the use of carbon on the same lines in 1882.

Iron is, of course, impossible as a support in the usual acid electrolyte, as it would very soon be dissolved up. C. T. Kingzett in 1882 took out a patent for electrodes with iron cores in an *alkaline* solution, but even then the iron appears to have required to be completely sheathed with lead to keep it out of contact with the electrolyte, and Swinburne in 1883 also found it impossible to prevent iron supports from being destroyed by local action with the peroxide. S. Kalischer, in 1884, proposed the use of iron coated with electrolytically-deposited lead peroxide in neutral solutions. J. Lea proposed to employ copper sheets or copper wire gauze coated with lead in 1882, and

FitzGerald advocated the use of copper for negative supports in 1890, as he maintained that this metal was not attacked by dilute acid if an excess of unoxidised spongy lead were always present—that is to say, if the electrode were never over-discharged.

Frequent references occur in later patents to the possible use of metals such as iron, copper or aluminium for supports in acid solutions, but very little is said as to how they are to be protected from the action of the electrolyte, except by completely encasing in a sheath of lead.

Active Material.

Although the active materials of lead cells are always the same, yet the raw materials from which they are prepared and the method of their preparation may differ considerably. The raw active material of Planté type electrodes is the surface metal of the support itself. According to Planté's original method, this was gradually attacked and converted into porous layers of lead and lead peroxide by subjection to a long and systematic series of charges, periods of rest and reversals in dilute sulphuric acid, and the object of all subsequent modifications has been to increase the rate at which the metal can be oxidised so as to reduce the time occupied and the cost. In 1881, Planté proposed to heat the electrodes during formation, and the same idea was put forward by C. F. Brush in 1883, while according to a patent taken out by H. O. Tudor in 1896 the formation may to some extent be accelerated by carrying it on in an electrolyte containing an extremely small percentage of sulphuric acid, but with these exceptions most processes consist either in subjecting the electrodes to some preliminary treatment which will rapidly oxidise them or leave them in a condition to be rapidly oxidised afterwards, or else in their direct formation in some special electrolyte. For these purposes all kinds of solutions have been proposed, generally dilute sulphuric acid with some oxidising agent added to it, but nitric acid has in nearly every case played a part in the few that have received any practical application.

In 1862 Planté patented a preliminary treatment in nitric acid (1 part of acid to 1 to 2 parts of water), and later in the

same year T. Parker and P. B. Elwell described the use of a mixture of dilute nitric and sulphuric acids in the same way. In 1886 P. J. R. Dujardin proposed a forming solution, consisting of dilute sulphuric acid with potassium or sodium nitrate added to it; and in 1890 L. Epstein obtained a patent for a method whose chief features were an initial boiling in very dilute nitric acid, about a 1 per cent. solution, followed by a drying process and then a formation in dilute sulphuric acid. Of preliminary treatments in the dry way, J. W. Swan's proposal to convert the surfaces of the electrodes into basic carbonate by a "white lead" process, and O. Schulz's use of sulphur to form sub-sulphides may be mentioned.

When Faure introduced the use of active materials not prepared from the support itself, he proposed to employ any suitable salt of lead as raw active material, but mentioned more specifically lead sulphate and lead oxides. In practice, minium mixed to a stiff paste with dilute sulphuric acid was at first adapted for both positive and negative electrodes, but litharge was soon substituted for the negatives, as a considerable saving in the amount of current required for their first formation could thereby be effected, and these two oxides have almost always been employed for pasted electrodes since. Other lead salts have been tried or proposed at various times, but have had a very restricted use. The same may be said of the attempts to improve on dilute sulphuric acid as a mixing fluid either by adding other materials to it or substituting them in its place. Every kind of substance, likely or unlikely, appears to have been tried: acids, alkalies and salts, both inorganic and organic, and a whole host of other organic compounds, including such familiar names as glycerine, sugar, amber, milk and gutta-percha. If not fluids themselves, they have been dissolved in some suitable solvent; but solid bodies such as charcoal or pumice stone, have also frequently been mixed with the paste to impart increased porosity to the active materials.

Those lead salts which are readily fusible constitute another class of raw active materials, but lead chloride is the only one of them which has received any practical application. In 1882-3 F. Maxwell Lyte obtained several patents for the use of lead chloride or other fusible lead salt, either casting

it direct on to a conducting support, or first casting it in pieces of a suitable size and shape, and casting a frame or grid round these afterwards, or employing it without a support at all. In 1885 A. Marchenay proposed to increase the mechanical strength of the cast chloride by fusing small proportions of zinc chloride or certain other chlorides with it, or by an admixture of asbestos fibre. The former of these methods appears to have been the one by which the use of lead chloride was first rendered commercially possible, for if cast in a pure state it cools so "short" and brittle as to be almost unworkable. In 1886 E. Andreoli further developed the processes for the preparation of active material from lead chloride and its employment in electrodes, and in 1889 C. Payen proposed to form the necessary percentage of zinc chloride by adding metallic zinc to the lead chloride when in a fused state. The details of manufacture are described still more fully in a patent granted to A. M. F. Laurent-Cély in 1890.

The deposition of active material from a solution of a lead salt furnishes yet another method by which it may be prepared. Spongy lead precipitated by zinc from a solution of lead nitrate or acetate was used by many of the early inventors. As far back as 1872 Planté considered and experimented upon the feasibility of accelerating the preparation of the layers of active material upon his electrodes by direct electrolytic deposition; and this probably constitutes the foundation for the statement sometimes made that Planté anticipated Faure in the employment of applied active material. A solution of lead oxide in caustic alkali appears to have always been the favourite electrolyte for a treatment of this kind. It was proposed by A. Muirhead and by J. M. Gérard-Lescuyer in 1882. In 1884 C. B. de Montaud formed both positive and negative electrodes in it, consolidating the deposited spongy lead by subjection to considerable pressure afterwards. Its use was also described by several other inventors later.

Many attempts have been made to prepare active materials of sufficient mechanical strength, durability and electrical conductivity, that they could be made up into masses of a considerable size without any support, and so used for complete electrodes. Amongst the earliest workers in this

direction were Brush, E. T. Starr, A. Tribe, E. Frankland and R. Tamine, and in nearly every instance they endeavoured to achieve success by consolidating the raw active materials under pressure. Maxwell Lyte's use of lead chloride with the same object has just been mentioned. In 1884 D. G. Fitz-Gerald took out the first of a long series of patents dealing with this class of active materials and electrodes, which were afterwards known as "Lithanode," and the term has since been largely applied to describe all plates of a similar kind. His first lithanode materials were prepared from mixtures of finely-divided lead and lead oxide with dilute solution of magnesium sulphate, moulded under pressure. In 1885 he substituted ammonium sulphate solution, or else mixed the lead compounds with the dry salt, and after compression treated them with water spray or steam; while in 1886 he introduced glycerine into his mixing solution. In 1893 he patented an entirely different process, in which litharge was mixed with a weak solution of a caustic alkali and then treated with carbonic dioxide gas, either by exposure to the air or other means. This broke up the combination between the lead oxide and the alkali, converting them both into carbonates and setting the mass.

Grid Supports.

In the first pasted plates of Faure, the supports for the active material were simply plain sheets of lead, upon whose smooth or roughened surfaces the oxides were laid; but it was soon found that they did not possess sufficient coherence and adhesion to remain in position of themselves without further assistance. Swan was the first to introduce the type of support divided up into a series of receptacles that served to contain the active material and hold it together. His plates, as illustrated in his patent taken out in 1881, very soon after Faure's original patent, were of two classes—cellular and grooved—which may be considered as the parents of innumerable modifications of after years. Fig. 1 shows his cellular support or grid, with hexagonal cells open right through from side to side, and flat walls at right angles to the surfaces of the plate.

Supports of very similar construction to those of Swan were described in patents applied for by Brush in the United States and E. Volckmar in France at about the same time, although in the former case the patent was not finally granted and published until 1886.

While such plates afford considerable support to the active material, there is nothing to prevent whole pellets of it from

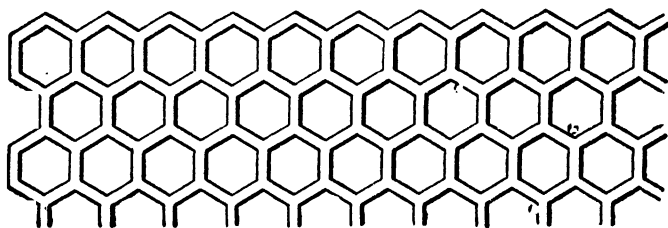


FIG. 1.—Swan's Grid.

coming away should they shrink or become loose, and in 1882 Sellon proposed to meet this difficulty by the use of grids with convex walls to the cells—that is to say, with holes or cells which taper inwards from either side, and so grip the active material they contain and hold it firmly in its place. His patent shows grids of a variety of cross-sections two of the most practical of which are given in Fig. 2. and one of

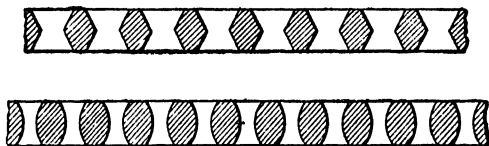


FIG. 2.—Sellon's Convex Grids.

these will be recognised as the familiar diamond section so largely used for grids ever since. Figs. 3 and 4 are early grids of this type; the first manufactured by the Faure, Sellon and Volckmar Co. in France, the second by the Oerlikon Co. in Switzerland.

From time to time various modifications of these simple forms of grid have been proposed to meet defects, either real

or fancied, to which they are liable. It was observed that the pellets of active material in grids with inward tapering cells

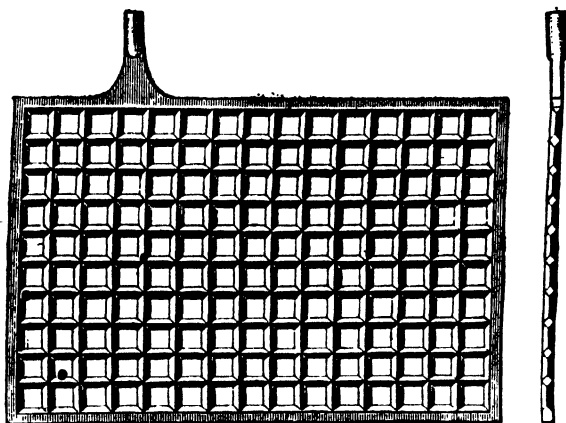


FIG. 3.—F.S.V. Diamond Section Grid.

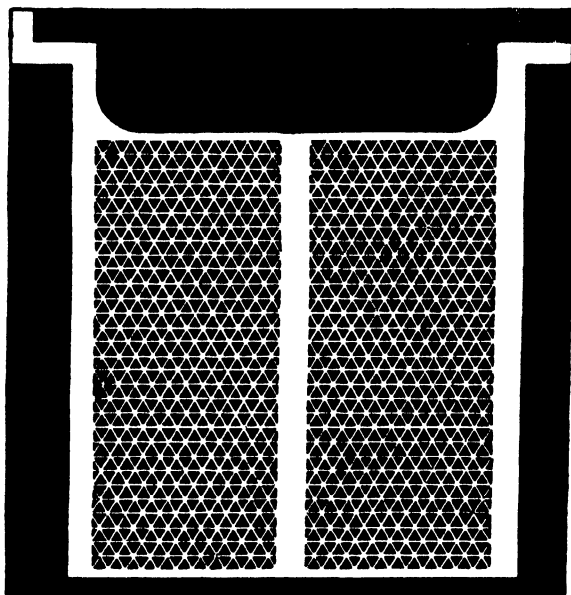


FIG. 4.—Oerlikon Triangular-holed Grid.

sometimes cracked across their centre or point of smallest diameter, in which case there was nothing to prevent the two halves from falling away on either side. The most obvious method of combating this fault was to reverse the taper of the cells, making them smaller at the mouth than at the centre by means of concave walls, provided some practical means of casting such undercut grids were available. Sellon did indeed, in his patent referred to above, illustrate a cross-section of one form of grid of this nature (see Fig. 5), but he made no



FIG. 5.—Sellon's Concave Grid.

comment upon it, nor did he suggest any means of overcoming the difficulties involved in its manufacture, and it was not until 1889 that the Electrical Power Storage Company patented a grid of somewhat similar design, and showed how it might be constructed by the use of special moulds. Even then, however, it was only possible to make two walls of each cell concave, the grid bars running in one direction having a cross-section such as is shown in Fig. 5, and the bars at right-angles, the ordinary convex cross-sections such as in Fig. 2. Previously to this, in 1887, C. L. Menges had patented a grid with V or gutter shaped bars (see Fig. 6), and had described special moulds for casting it. This



FIG. 6.—Menges' Grid.

form of grid bar also furnishes holes having two convex and two concave sides, and although they are not tapering, their cross-sectional area being the same throughout, yet they answer much the same purpose, for, provided the concave side of the bars is kept uppermost, the half pellets of active material would have to rise upwards before they could fall out.

In 1893 M. Hartung proposed to construct grids with triangular section bars, half of which had their apex towards one face of the plate, and half, at right angles to the first, towards

the other face. By this means each cell or hole had two walls tapering in one direction and two in the other.

To obtain supports in which *all* the cell walls taper outwards other means had to be adopted. One was to cast them with the usual flat or inward tapering cell walls, and then turn over their outer edges by pressure. H. O. Tudor patented such a plan as applied to his grooved supports in 1887, and in 1888 B. M. Drake and J. M. Gorham proposed to treat grids in a similar way by passing them through special burnishing rollers. Fig. 7 shows a diamond framed grid in cross-section

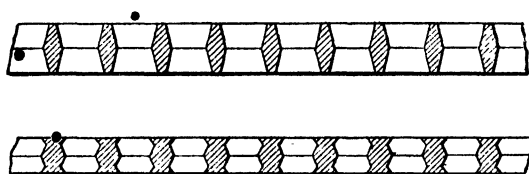


FIG. 7.—Drake and Gorham's Burred-over Grid.

before and after this treatment. C. D. P. Gibson also patented a somewhat analagous method shortly afterwards. In this instance grids were first punched or cast with flat walled holes and a rim of metal standing up round each, next this was partly turned over by stamping, and finally, after the cells had been filled with active material, the plate was passed through rollers which reduced it in thickness and still further closed up the apertures. These three stages are shown in Fig. 8, and it

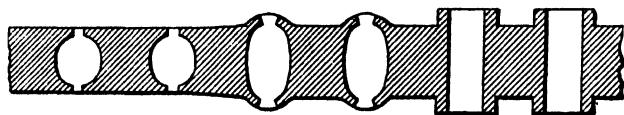


FIG. 8.—Gibson's Grid.

will be noticed that the mouths of the cells are reduced to the very smallest proportions. In another form of grid described in the patent, holes were stabbed diagonally in a plate, and the burrs thus raised turned over by rolling as before.

Figs. 9 and 10 show, in plan and cross-section, a portion of a grid described by I. Peral in 1890. The former represents the grid as cast, but some of the diamond section-bars running in

one direction have notched edges, which are flattened and turned over right and left by stamping, so that finally it assumes the appearance of Fig. 10. This construction also illustrates a device frequently adopted for getting a large amount of active material into a light support. A shallow grid is surrounded by a frame much deeper than itself, and sometimes, as in the present instance, is also crossed at intervals by bars of the same depth as the frame to further strengthen it.

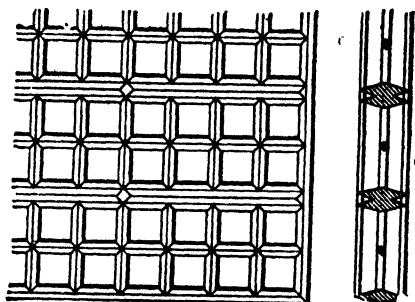


FIG. 9.—Peral's Grid (as cast).

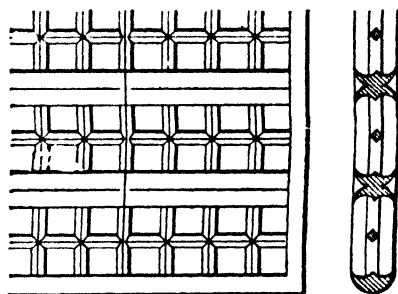


FIG. 10.—Peral's Grid (completed).

A second method of producing grids with undercut cell walls was to place two similar grids of triangular section back to back, with the broad bases of their holes inwards, and then join them together by bolting, burning, or other means. Provided the ribs and apertures of the two grids coincided properly, a single grid of twice their thickness was to all appearances obtained. The bars of the component grids

need not necessarily be of triangular cross-section, but were more often trapezoidal, and tapered from surface to surface. Fig. 11 shows a plan and cross-section of one of the earliest grids of this kind, manufactured by the Faure, Sellon and Volekmar Company in 1883. In the same year Maxwell-Lyte proposed a similar construction, but he placed his pellets of active material, which were of lead chloride previously moulded to the right shape, in position in the apertures before joining the two grids together. Grids in two pieces have also

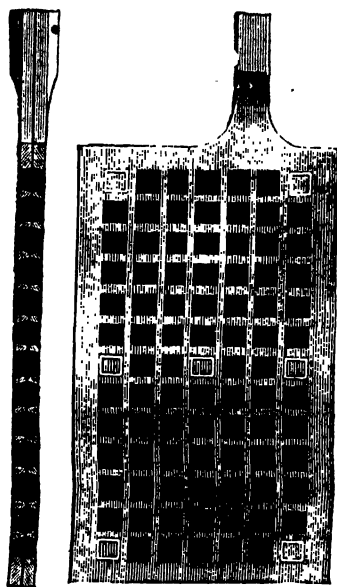


FIG. 11.—F.S.V. Two-part Grid.

been used by P. L. M. Gadot, M. Jacquet, F. M. A. Laurent-Cély, and many others, but none of them contain any novel features of much utility beyond what have been described. Grids in three pieces have occasionally been constructed, as for instance that of P. Germain in 1892, in which the middle grid was left unpasted to hold a supply of electrolyte.

Another rather ingenious but not very practical method of gripping the pellets of active material, proposed by T. Harris and H. F. Cameron in 1889, was to prepare grids

with round holes, and then, as it were, corrugate their walls by screw-threading them. Fig. 12 shows a single hole treated in this way.

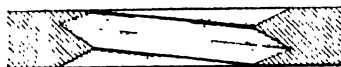


FIG. 12.—Harris and Cameron's Grid.

The "claw" grid of the Electrical Power Storage Company, patented by F. King and E. Clark in 1892, has the same common object as those just described, of providing additional hold on the active material, but beyond this it is specially

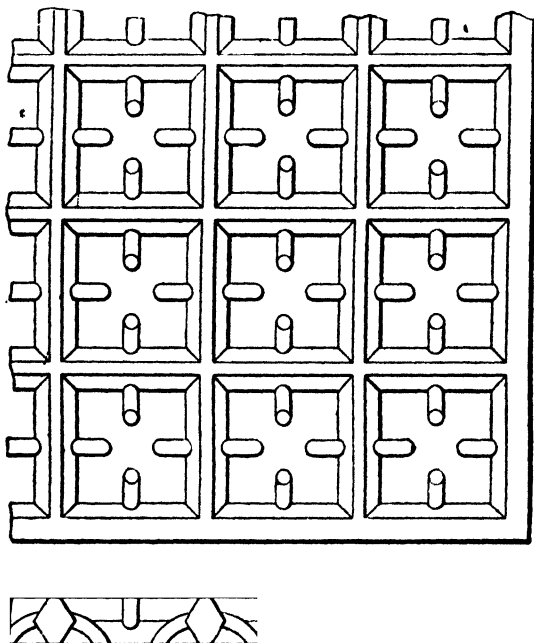


FIG. 13.—King and Clark's 'claw' Grid.

designed for negative supports to cope with the *shrinkage* of the active material that in the course of time always occurs there. Fig. 13 shows a portion of such a grid in

plan and cross-section. The walls of the cells are of the usual diamond section, but from the centre of each wall small round pins project inwards and curve towards the surfaces of the grid, two one way and two the other. The purpose of this construction is that the contraction of the active material may cause it to bind more closely on the pins, and so maintain a good contact with its support even should it draw away from the sides of the holes.

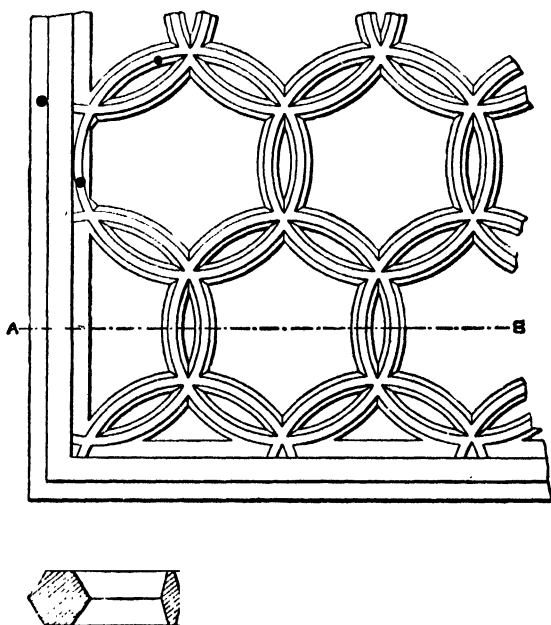


FIG. 14.—Farbarky and Schenek's Grid.

A trouble to which electrodes of the grid type were even more liable some years ago than is the case at the present day was that of buckling and distortion of the support, or in extreme cases its fracture and tearing asunder. This action is mostly confined to the positive electrodes, and is due to the abnormal expansion of the active material contained in the holes in the support, and consequent pressure put upon the surrounding walls.

In 1886 S. Farbarky and S. Schenek proposed to overcome this difficulty by constructing grid supports in which the cells containing the active material were surrounded by smaller apertures left empty, the idea being that as the active material expanded, the enclosing walls would give and bulge into the unfilled spaces, and so relieve the strain that would otherwise be put upon the whole electrode. Fig. 14 is a cross-section and plan of the form of support illustrated in their patent, consisting of hexagonal holes for the active material, divided from each other by oblong slots with curved sides.

In 1889 G. E. Heyl proposed to construct electrodes on very similar lines, the grids shown in this instance containing rectangular cells surrounded by narrow grooves, either passing right through the support or divided into two by a thin wall in the middle. Fig. 15 shows a cross-section and plan of a

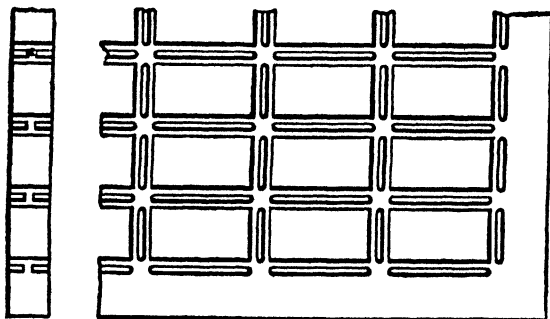


FIG. 15.—Heyl's Grid.

portion of a grid constructed according to the latter method. Heyl also suggested turning in the walls of the cells after they were filled with active material, so as to hold it more firmly in position.

Double Grids.

Some of the grids already described are double, in the sense that they have to be built up of two separate grids in order to overcome structural difficulties involved in their direct manufacture all in one piece, but they closely resemble single grids when completed. There are, however, a considerable number of grid electrodes which may or may not be constructed in one

piece, but which, in either case are double, in the sense that they present two distinct gratings or lattices on either side of the plate. These two gratings may be close together, but with their cell walls crossing one another and only coinciding at certain points; or they may be a little distance apart and held together by intermediate studs or ribs, or merely by a surrounding frame common to both of them.

Humphreys' support, patented in 1882, consisted of a number of bars of oval, diamond, or other section, set diagonally, after the manner of the laths in a Venetian blind, and cast in a frame (see Fig. 16). These could be used either

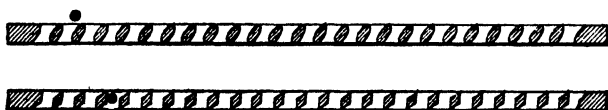


FIG. 16.—Humphreys' Grid.

singly or two of them together as double grids, and with the bars either parallel or at right angles to each other (see Fig. 17). In the illustration of the bars at right angles it

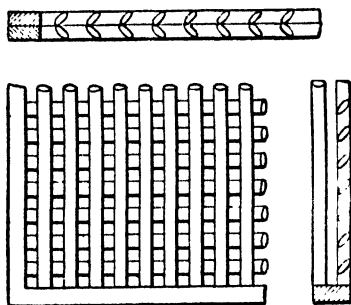


FIG. 17.—Humphreys' Double Grid.

will be noticed that the two sets do not touch each other, but have a space left between them to allow for a larger proportion of active material.

Gibson's support is constructed by punching and pressing out rectangular tongues alternatingly on either side of flat lead plates, so as to stand at an angle of about 45deg. Two such plates are then joined back to back, either with the

tongues interlocking, as shown in Fig. 18, or with their tips bearing against each other, as in Fig. 19.

J. S. Sellon patented a double grid in 1889, and it may be remarked in passing that, so far as the mechanical construction of pasted electrodes is concerned, there are not many possible directions for improvement which Mr. J. S. Sellon does not appear to have investigated with more or less



FIG. 18.



FIG. 19.

Gibson's Double Grids.

success. Fig. 20 shows a portion of this grid in plan and cross-section. The cells on either side do not coincide, but are so disposed that every cell opens into four others on the opposite side, and in this way continuity of the active material is maintained throughout. The result is just the same as if an ordinary grid with diamond section bars were split down

the middle, and one half displaced diagonally over the other by half the width of one of the holes.

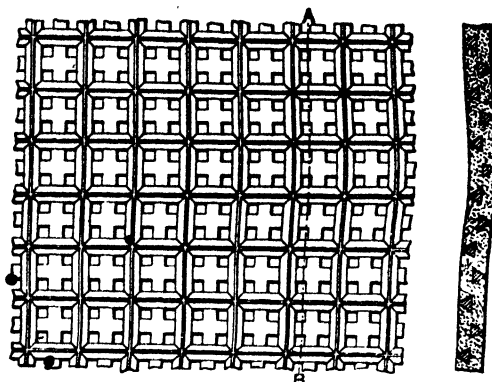


FIG. 20.—Sellon's Double Grid.

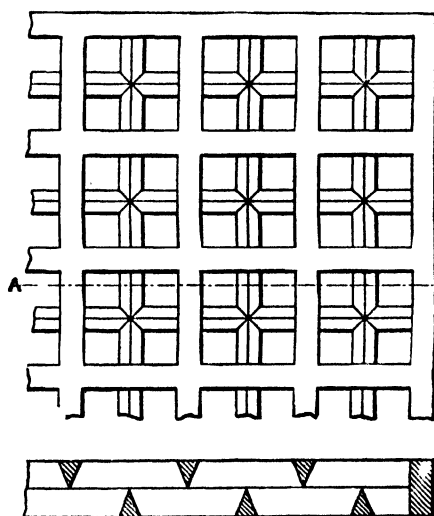


FIG. 21.—Correns' Grid.

An ingeniously constructed grid of this kind is that patented by E. Correns later in the same year. His first plan was to

superimpose two thin grids with square holes and parallel walls, placing them together so that the holes in each grid came centrally over the grid bars of the other. A stamp was next passed through the holes in one of the grids, and the bars of the grid underneath pressed into the shape of a triangle, with the apex inwards; then the grids were turned over, and the other bars stamped in the same fashion. By this method a good bearing surface was obtained at every point where the bars of the two grids intersect, which would not have been the case if two grids with triangular bars were merely placed back to back. Finally, the two grids were united by burning or other means.

In a later patent this method was greatly improved upon and simplified by casting the complete grid at one operation in special interlocking moulds. Fig. 21 shows a plan and cross-section of a portion of such an electrode. It will be observed that in its general appearance it is very similar to Sellon's grid; but in the latter the bases of the triangular bars are inwards, giving inward tapering cells, while in Correns' grid the cells taper outwards. Also in 1889, C. Beyer and G. Hagen patented a form of grid support consisting of two half-grids held rigidly some distance apart by means of cross-connecting stays or studs and an outer frame, all cast in one piece with the grids. The holes in the two grids could either correspond or could overlap each other. Both methods are shown in Fig. 22. The casting of the complete support,—*i.e.*, two grids and cross-connections all in one piece,—appears not to have been a very practical affair at first, as it involved the use of cores of sand which would have to be re-made each time; but in 1894 the same patentees described and patented moulds which enabled them to cope with this difficulty, and to obtain cross-bars not only of a rectangular section, but also of an undercut or triangular section. Portions of grids of the latter kind are illustrated in Figs. 23 and 24, and it will be noticed that in one instance a triple lattice is provided. In 1892 E. Andreoli patented an electrode which, when completed, resembled those just described, but was constructed in an entirely different manner. Two separate grids were held some small distance apart in a mould by means of brass pins passing through holes in both the grids. The grids themselves and the space between

were then filled in with molten lead chloride, and when this had solidified the pins were withdrawn and molten lead run into the holes left, thereby effecting a direct metallic connection between the two grids and binding them rigidly together.

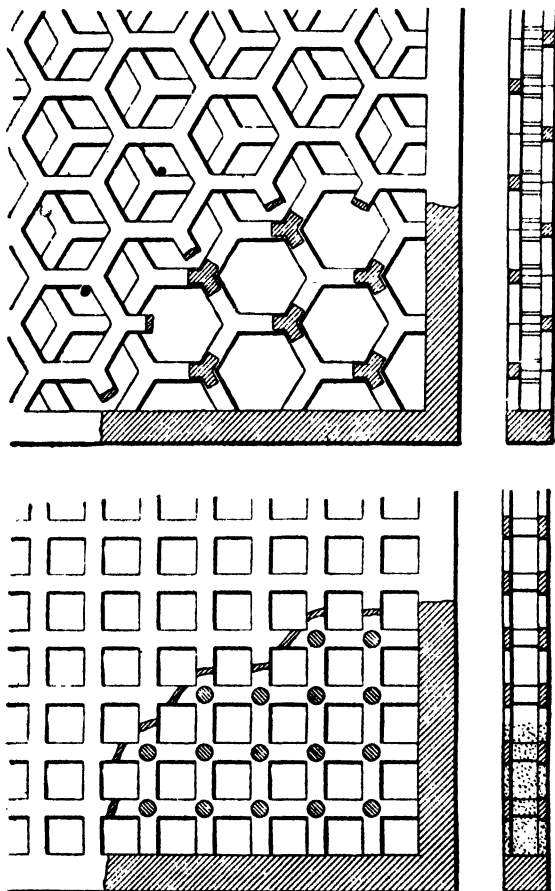


FIG. 22.—Beyer and Hagen's Double Lattice Grids.

In all these supports the special object aimed at is to reduce their weight in proportion to that of the active material, for besides the active material held in the grids themselves there

is a complete layer of it between the two, except where the cross-connecting studs pass through.

Fig. 25 gives cross-sections of some types of support patented by King and Clark in 1896. Here the two lattices are joined at intervals by crossbars or strips instead of by studs or pins. In addition, there is an intermediate partition

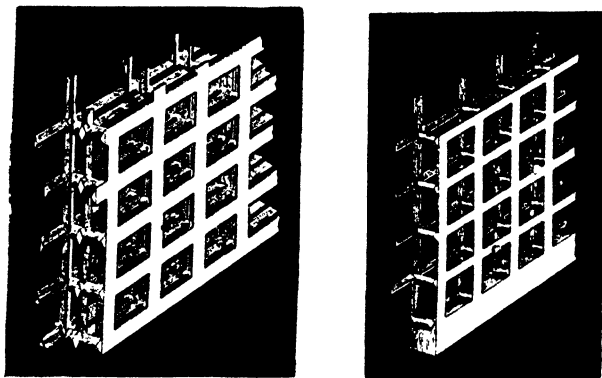


FIG. 23.—Hagen's Grids.

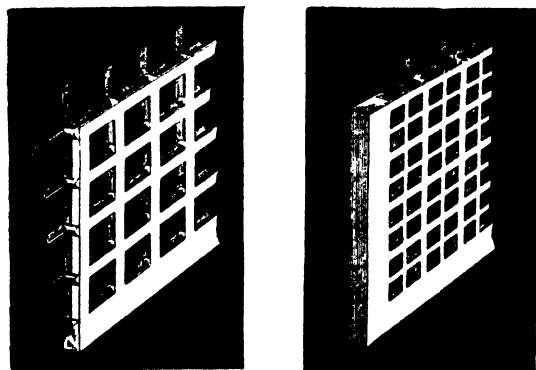


FIG. 24.—Hagen's Grids.

which passes centrally between the lattices in the first section shown, or runs obliquely from one to the other and from crossbar to crossbar in the next two. There is also another modification in which the lattice upon either side is not continuous, but only in alternate sections joined by crossbars,

and there is no partition between them. The sections of the lattice are cast with curved faces, but are afterwards flattened out and the crossbars thereby set obliquely to them, so that the support finally appears as in the last cross-section.

F. W. Schneider has also patented supports with various arrangements of partitions and crossbars between the two

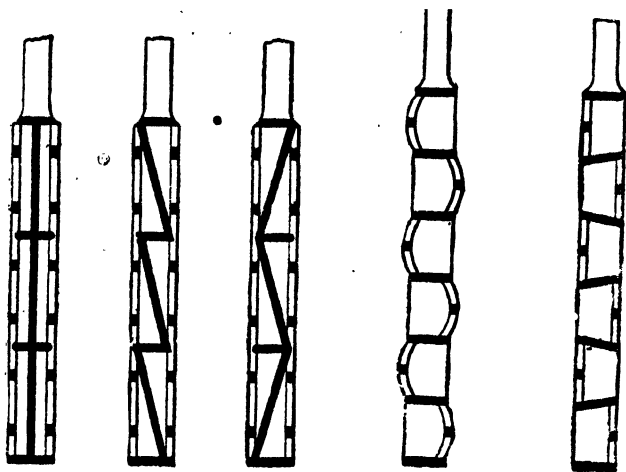


FIG. 25.—King and Clark's Double Lattice Grids.

faces, and A. Lehmann constructs them with grids in alternate sections, but only connected by studs at intervals and not by continuous bars.

Recessed and Pocket Supports.

These have a central backing or web of solid metal covered on either side with recesses, which most usually take the form of cells or grooves. Brush described such cellular electrodes under the name of "honeycombed" plates in his patents of 1881 and onwards, and similar supports were also proposed by G. Giovanni in 1890, K. F. Schöller and R. H. Jahr in 1891, and J. E. Hofmann in 1893; but none of them present any special features, their design being that of the ordinary types of grid plus a core of lead down their centre.

Grooved supports intended for pasting with lead oxides were patented by both Swan and Brush in 1881. In 1895

A. Khotinsky obtained a patent for ribbed supports, prepared in strips by forcing lead under hydraulic pressure through suitable dies. Fig. 26 gives cross-sections of some of his

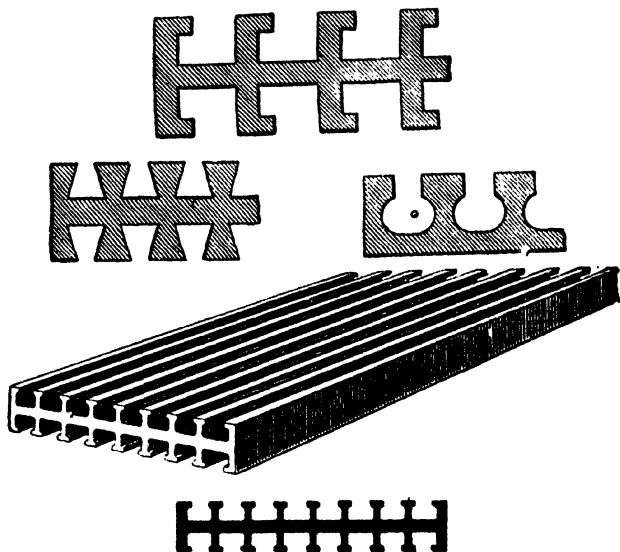


FIG. 26.—Khotinsky's Supports.

earliest designs, and shows a portion of a strip of the shape afterwards adopted. The strips could be used either singly, as illustrated in Fig. 27, or a number of them mounted in a

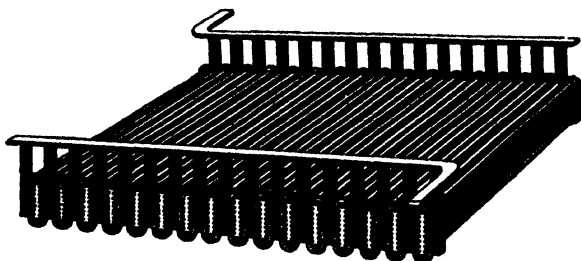


FIG. 27.—Khotinsky's Single Strip Electrodes.

frame to form a complete electrode, but in every case the ribs ran horizontally. In 1887 Tudor proposed a grooved support whose ribs were burred over by rolling after the active material had

been inserted; and in 1888 J. T. Van Gestel also described a support in which ribs projected at right angles from a solid core plate, but after pasting it was passed through rollers, and the ends of the ribs turned up parallel to the plate, so as to convert them into shallow troughs.

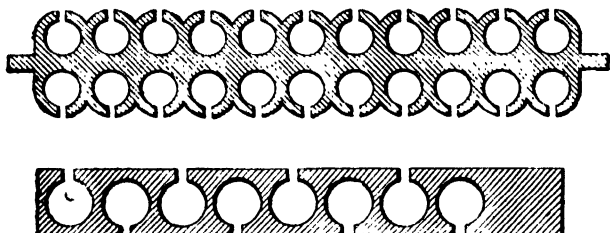


FIG. 28.—Logan's Slotted Tube Supports.

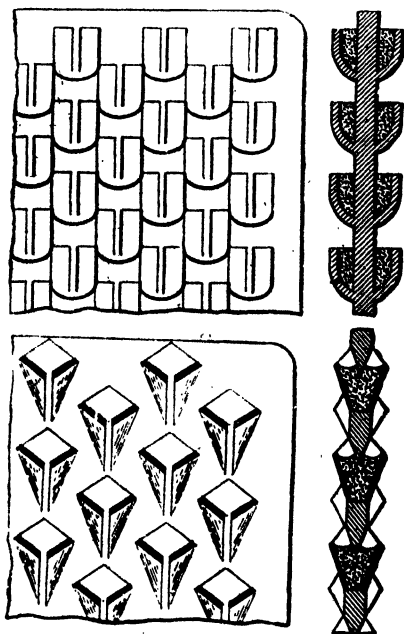


FIG. 29.—Logan's "Pocket" Supports.

In 1889 C. H. Logan proposed to pack the active material in supports containing a series of vertical cylindrical receptacles side by side, like rows of slotted tubes cast all in

one piece. Two forms of this support are given in cross-section in Fig. 28. These tubes were open at the top and closed at the bottom.

In another type of support, two examples of which are shown in Fig. 29, he still further subdivided the active material in small slotted pockets. In the one construction the pockets on either side of the electrode are separated by a solid central core plate, but in the other corresponding pairs of pockets open right through, so that this support partakes very much of the nature of a grid.

With the exception of those just described, grooved or ribbed supports have chiefly been employed for electrodes of the Planté type, and the rest of them will be dealt with under that heading.

Studded Supports.

Another class of supports also possessing a central dividing plate is that in which numerous pins or studs project on either side instead of ribs. Sellon illustrated one of this kind in 1881, and proposed to burr over the ends of the pins in order to give a better hold upon the active material in between them. Brush included studded plates amongst the various designs claimed in his patents of the same year. J. Pitkin described a very similar construction in 1886, and C. Pollak in 1889 patented a rolled support of the same type, which is manufactured on a commercial scale in Germany.

A rather curious studded plate was patented in the United States in 1883 by E. T. Starr. In this instance the pins were perforated and the circular walls remaining then turned over and spread out by pressure or other means.

Tube, Trough, and Bar Electrodes.

A variety of supports have been proposed which can hardly be called grids, but in which the active material is contained in a series of cellular bars or perforated tubes or open troughs, generally arranged vertically if of the first kind, or horizontally, if of the two latter kinds. They usually have to be built up of a number of separate pieces united together by a common frame or bars, and it is a characteristic feature of most of these electrodes that spaces are left in them for the electrolyte

to circulate through and obtain proper access to the active material.

In 1881 Sellon proposed to construct electrodes by placing a number of perforated lead tubes filled with active material close alongside each other and then casting a frame round them, as shown in Fig. 30.

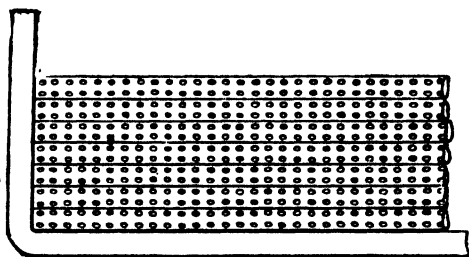


FIG. 30.—Sellon's Tubular Electrode.

In the same year he also described a support, consisting of a number of strips of perforated lead, set edgeways, with small spaces between them, and then cast in a frame. L.

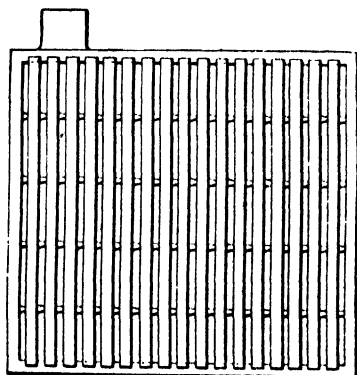


FIG. 31.—Epstein's Strip Electrode.

Epstein proposed a somewhat similar form in 1887, but in this instance the strips were provided with projecting pins or ridges to keep them from close contact with each other. This electrode is illustrated in Fig. 81.

In 1887 Van Gestel constructed electrodes from a single length of tube filled with active material and coiled up spirally. It was then subjected to pressure to flatten the tube to a rectangular shape, and perforated. A somewhat similar construction was patented by T. M. Foote in 1890, but he bent the perforated tube backwards and forwards on itself to form a rectangular plate of the desired dimensions. Adjacent bends of the pipe were burned together in order to strengthen the electrode and reduce its resistance.

In the same year J. Pitkin and H. C. Holden patented their "ladder" electrode. This consisted of a number of open troughs of channel section lead placed vertically above each other with small spacing pieces in between them, and then

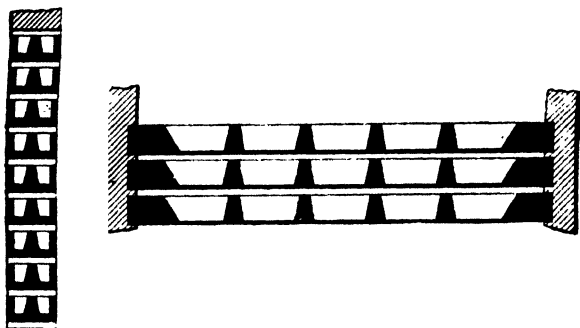


FIG. 32.—Pitkin and Holden's "Ladder" Electrode.

united by casting on two vertical side bars, after which the spacing pieces were withdrawn. Fig. 32 shows a portion of an electrode of this kind in vertical and longitudinal section. The active material is placed in the troughs before they are connected together. Pins project into it at intervals from the bottom of the troughs for the purpose of ensuring a better contact with the support. In a modification of this support, patented in 1893, Pitkin greatly simplified its construction. The troughs were made with solid ends and projecting feet of the same depth as the spacing required between the troughs. To build up the electrode, these troughs simply have to be piled on each other and burned together down the two ends without casting on any extra metal, the feet forming the

spacing pieces, and the solid ends, the main connecting bars (*see* Fig. 33).

H. Hauser described various designs for electrodes of this class in 1891, and a patent for somewhat similar plates was obtained by C. F. Winkler in the United States in 1892. The troughs



FIG. 33.—Pitkin's Trough Electrode.

in this instance were of a V-section, and could either be of metal or of some insulating material with conducting rods lying along their bottom. The former construction is shown in Fig. 34, the latter in Fig. 35, and it will be noticed that

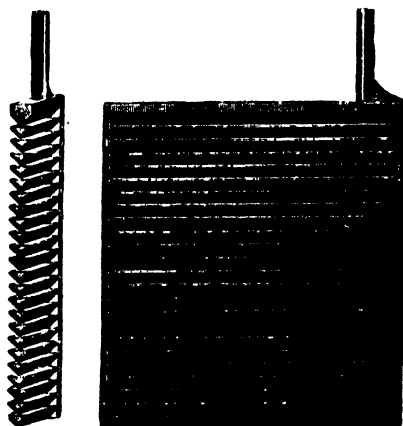


FIG. 34.—Winkler's Metallic Trough Electrode.

not only the troughs but the whole frame of the electrode is of insulating material, the rods from the troughs being connected to one main conducting bar which passes up one side. Electrodes differing in details of design from those already

described were patented by F. W. Schneider in 1896, but their main features are the same,—*i.e.*, perforated tubes or open troughs set in a frame.

H. W. Headland's support, patented in 1892, might also be described as built up of a number of lengths of perforated tube, only the perforations are so numerous and of such a size that the tubes resolve themselves into long narrow rectangular frames or grids, consisting of four uprights joined

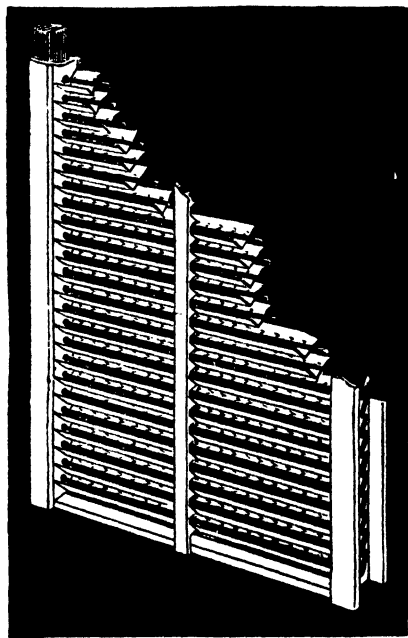


FIG. 35.—Winkler's Insulated Trough Electrode.

together on all sides by numerous cross-bars. To constitute an electrode a number of these bars are set parallel to each other in a frame, a small space being left between each to allow for the electrolyte to circulate round them on all sides.

According to a later design of grid bar, the four uprights are replaced by eight—four outer and four inner bars—of much slighter construction, and joined together at intervals

by thin horizontal ledges or shelves, so that altogether considerably more space is provided for active material than in the earlier type.

Moulded Pellet Electrodes.

The class of electrodes in which the active material is prepared and shaped in separate pieces before attachment to the support, generally by casting the latter round them, do not present any very novel features so far as the design of the grids is concerned. In pasted electrodes the grid determines the shape, size and disposition of the pellets of active material, but here of course the reverse is the case, and the pellets and their spacing determine the grid. A description of the grid resolves itself therefore into one of the arrangement of the active material. In this method of manufacture it is just as easy to construct the supports with undercut or concave cell walls as of any other design, merely by using pellets with a corresponding convexity on their edges, and most of these grids will be found to possess this feature.

Maxwell Lyte appears to have been the first to propose the construction of plates in this way in connection with the use of lead chloride as active material. He patented the process in 1883, and specified that the pellets or studs should be provided with collars or projections on their edges of such a form as to be retained in place by the support. Besides casting a grid round the studs, he also proposed to use two half-grids with taper cells, and to burn them together after the pellets had been inserted, while, according to a later patent of the same year, in order to secure better conductivity, he placed a solid metal plate between the two half-grids against which the broad bases of the pellets rested.

Epstein described some electrodes of the same class in 1884, but in this instance rectangular pellets of active material were packed close together, and the support cast either through holes in their interior or in recessed grooves in their edges, so that none of it appeared at the surface of the plate. Fig. 36 shows a section of a plate of the former description with round holes passing through the centre of the pellets at right angles to each other, and one of the latter kind with triangular grooves round their edges. The single pellet illustrated has a

semi-circular groove round it, but the channels running across its surface are also intended to be filled with metal, which will constitute an additional conductor and support.

In 1886 A. Reckenzaun described electrodes having frames cast round pellets of active material, the form of plate he preferred containing cylindrical rods about 1 in. long and $\frac{1}{4}$ in. in diameter. Their curved surfaces projected on both sides of

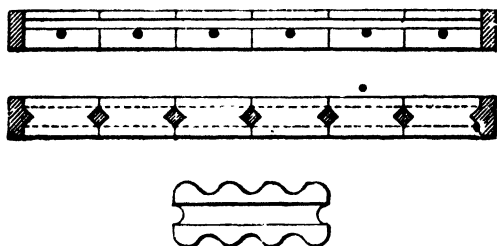


FIG. 36.—Epstein's Moulded Pellet Electrode.

the plate, which was about $\frac{1}{4}$ in. thick. Fig. 37 shows such a plate in cross-section, and Fig. 38 gives a general view. In the same year E. Frankland patented an electrode very similar to that of Reckenzaun, but the cylinders of active material were flattened down to form convex-edged tablets of the same thickness as the frame to be cast round them. Also in 1886, W. W. Beaumont proposed to apply the same method of construction, more especially in connection with active materials of the "lithanode" type, which had just



FIG. 37.—Reckenzaun's Electrode.

recently been introduced by FitzGerald. Fig. 89 shows two of the various forms of pellets described, the one simply having convex or bevelled edges, and the other projecting pins in addition, to key it still more securely into the frame. Either small pellets with flat faces could be used, or larger ones with a network of channels crossing their surfaces, and holes passing from side to side at their points of

intersection, as illustrated. The object of this latter arrangement is to keep down the weight of the frame as much as

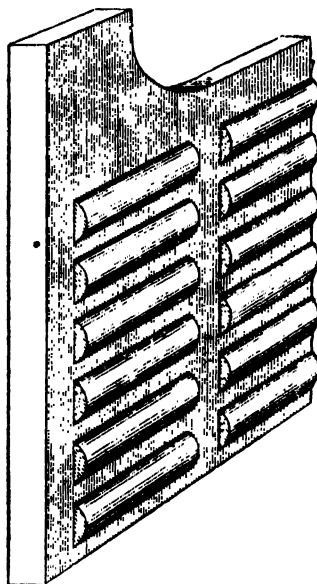


FIG. 38.—Reckenzaun's Electrode.

possible, while at the same time providing efficient support and conduction to all parts of the active material.

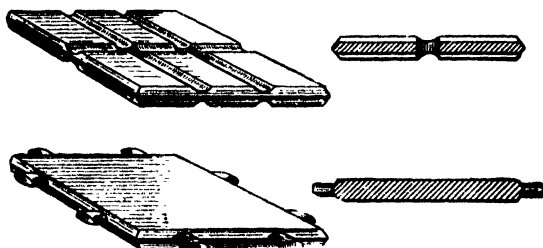


FIG. 39.—Beaumont's Moulded Pellets.

In 1887 Laurent Cély applied for a patent for an electrode similarly constructed to those already described, and using

lead chloride for the raw active material; but this was successfully opposed and consequently not granted. In 1890, however, in conjunction with I. A. Timmis, he obtained a patent for the same kind of plate, in which very full details are given regarding the processes of manufacture. Fig. 40 gives a plan of one of the forms of pellet illustrated, and two typical cross-sections, from which it will be seen that they embody very

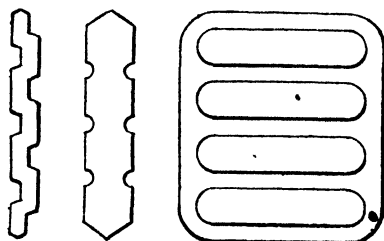


FIG. 40.—Laurent-Cély's Cast Chloride Pellets.

similar features to those of Epstein and Beaumont, already described—that is, bevelled or convex edges to afford a firm grip to the frame, and cross-channelling of their faces to further subdivide the exposed surface. In later forms of the plate, however, these surface bars were largely abandoned.

Protected Electrodes.

All those electrodes which are contained or surrounded by diaphragms, envelopes, or wrappings of some porous or perforated non-conducting material to assist in maintaining the active material in its place may be termed “protected,” in contradistinction to those in which the usual metallic support is deemed sufficient for the purpose. The above term has only been introduced into storage battery nomenclature within the last few years, but this type of electrode is as old as storage batteries themselves, and dates from the first practical cells ever constructed, the idea no doubt being taken from the porous pots and various arrangements of porous fabrics used to maintain the depolarising agents round the electrodes in primary cells.

Although protective coverings may be applied to almost any kind of electrode of whatever construction, their use is

frequently accompanied by some special design of metallic support and arrangement of active material of such a nature that it would be quite impracticable to employ the electrodes without the protection intended to go with them. This applies more especially to those electrodes in which the support is reduced to the very slightest proportions, and the protection itself is largely relied on to give sufficient mechanical strength and rigidity to the electrode as well as to maintain the active material against it.

In many instances the details of the methods of protection also necessarily involve a consideration of the means used for separating or keeping the electrodes apart, the two objects frequently being served by one and the same arrangement of parts.

For example, the electrodes in Planté's original cells constructed before 1872 were separated and at the same time protected by layers of flannel pressing closely against their surfaces, but this plan was afterwards abandoned in favour of ebonite strip separation.

Faure's first form of electrode was a porous pot which contained and held up the material round a central conductor and in his first British patent, in 1881, he mentioned the use of layers of felt, asbestos, &c., between the electrodes (a "series" battery in this instance having flat plates coated with oxides), but more with the object of preventing splashing and producing a sort of semi-dry battery than of supporting the active material. Faure soon found, however, that his active material would not for long retain its position on the support unprotected and merely by its own cohesion and adhesion, and accordingly a few months later he patented methods of attaching porous coverings to the plates by riveting, stitching, cementing, &c. Fig. 41 shows one of these arrangements, in which the three layers,—*i.e.*, lead backing, active material, and protective covering—are all held together by numerous rivets. Another plan described was to merely lay the sheets of porous material on the surfaces of the plates, and then to press them closely against open-work frames or trellis of wicker placed in between, which served both as separators and to hold the protective sheets in position. This method is interesting, as being closely akin to various

arrangements for protecting electrodes of very much more recent date.

From this time onwards for the next few years all the descriptions and specifications of new types of plates and cells abound with references to and particulars of various arrangements of porous pots and plates, parchment envelopes, wrappings of flannel, felt, and so on, for both positive and negative electrodes. The more practical of these are described below, but the majority of the materials then used were not capable of enduring in the acid for any length of time

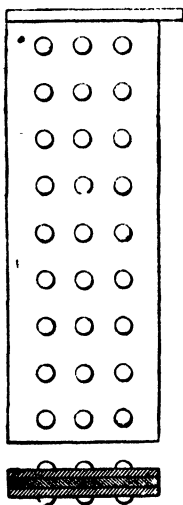


FIG. 41.—Faure's Protected Plate.

without suffering disintegration or deterioration, and this fact, coupled with the improvements effected in the design of the metallic supports, and the better coherence and durability obtained in the active material, led gradually to the almost total disuse of protection for some years. However, in 1890, or a little earlier, the ever-present need for light cells of large capacity, capable of giving higher rates of discharge and generally withstanding heavier work without depreciating too rapidly, caused attention to be once more turned to protected electrodes as a possible solution of the problem by

enabling larger quantities of active material to be placed and retained against the support than could otherwise be done.

During the last few years a considerable number of protected electrodes have been designed, and some of them put to practical use on a commercial scale, while at the present time the tendency to apply protection to electrodes of almost any and every type is nearly as strong as it was 15 years ago, but generally speaking the later arrangements for protection differ but little, if at all, from the earlier ones.

The use of porous or perforated containing cases of some non-conducting material was described by A. Tribe in 1882 and Fitzgerald in 1883. Also in 1882 A. P. Price proposed

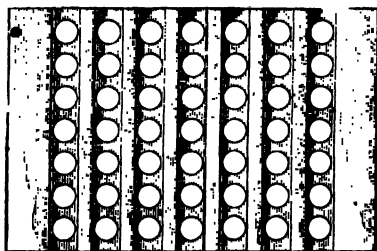


FIG. 42.—Howard's Grooved Wood Separator.

to employ sheets of indiarubber sponge as a material for protective separators, and G. L. Winch used sheets of cork or pith in a similar way. In the same year Pitkin enclosed his electrodes in a complete case of ebonite made up of a marginal frame and two perforated plates applied to either face. The perforations sloped obliquely upwards towards the outer faces, in order to diminish the liability for the active material to fall out through the holes. An alternative construction was to replace the perforated sheets by a series of thin strips set obliquely, like the laths of a venetian blind, by means of slanting grooves in the surrounding frame into which they fitted. He also introduced some other modifications on the same lines a year or so later. In 1883 Sellon employed porous tiles either flat, corrugated or perforated, as protective

separators between the plates, and he also proposed a kind of wood matting, consisting of a number of parallel rods of wood held closely together, for the same purpose. In 1884 G. Howard described a form of wood separator, flat on the side in contact with the positives, grooved on the other, and with large perforations passing through the grooves, as shown in Fig. 42.

Plate and Sheet Protection.

In 1887 E. E. Vaughton proposed to use porous plates pressed hard against the surfaces of the electrodes by means of wedges between them. The metallic support consisted of a perforated plate with a raised frame all round it. In 1889 C. B. Askew and J. K. Pumpelly, in a patent for a horizontal form of cell, described the use on the faces of the electrodes of asbestos sheets held apart and in position by open-work frames of interwoven leather strips to allow for the circulation of the electrolyte, thus very closely following the lines of Faure's wicker-work separators. An alternative method was to use porous plates ribbed on one side or flat plates held apart by ribbed separators.

In 1891 the Hess Electric Storage Company patented a compound protection, consisting of a layer of glass wool against the face of the electrode, and itself supported by a perforated plate or grid of rubber or similar material.

In 1892 H. H. Lloyd proposed to protect the surfaces of positive plates with sheets of ebonite or other insulating material perforated with clusters of holes opposite the pellets of active material. These latter were prepared from chloride of lead and of a fair size. The sheets were held up to the faces of the plates by rubber bands. The expressed object in this instance was not merely to maintain the active material in position, but primarily to protect the support or frame from electrolytic action, it being assumed that those parts covered by the solid portions of the protective sheets will offer more resistance, and so divert the action on to the active material.

Fig. 43 shows in elevation and cross-section a portion of an electrode protected in this manner, a part of the ebonite sheet being removed to exhibit the construction of the plate itself. In another patent in the following year Lloyd

considerably modified the above arrangement and also introduced a form of compound protection. The positive plates were first wrapped in a sheet of woven asbestos and a perforated plate of ebonite then placed on either side. The perforations were now, however, of the same size as the pellet



FIG. 43.—Lloyd's Perforated Sheet Protection.

of active material and so arranged as to come directly over them, while the ebonite plates were of sufficient thickness to form separators, the negatives pressing close against their other faces, but to allow for circulation of the electrolyte the

ebonite was vertically grooved on both sides. Fig. 44 gives a vertical and horizontal cross-section of a positive electrode protected in this way together with the negative electrodes on either side of it. Any number of electrodes could be similarly mounted and held together in one rigid mass by means of rubber bands or other clamping devices.

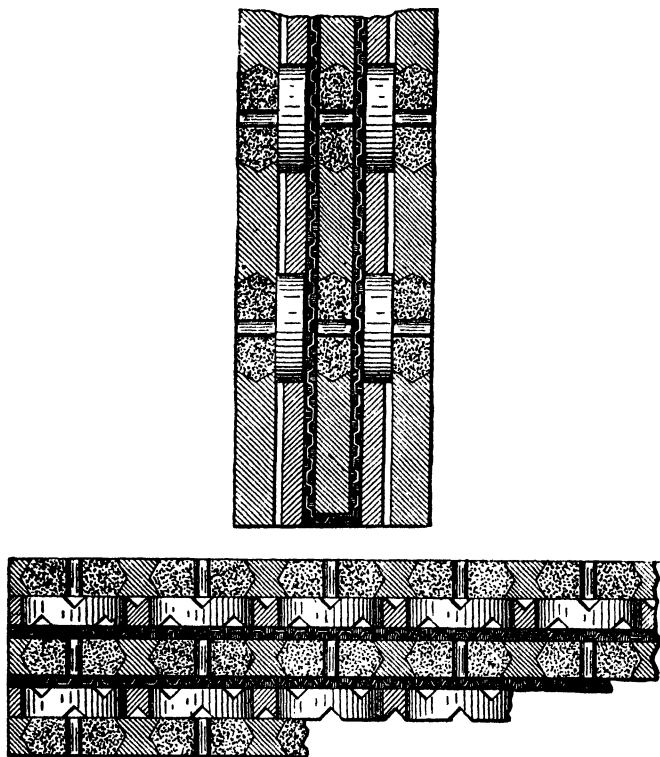


FIG. 44.—Lloyd's Asbestos and Ebonite Grid Protection.

This arrangement is of interest as being the basis of the protected type of cell of the Electric Storage Battery Company in the United States and the Chloride Electrical Storage Syndicate in England, and which was considerably used here at one time.

In 1890 Hatch made use of grooved separators of porous earthenware, but filled his positive and negative active

materials into either side of the separators themselves, drawing off the current by means of plain sheets of lead placed in between them. Fig. 45 shows a set of zigzag separators mounted in this way. In a more recent design two separators,

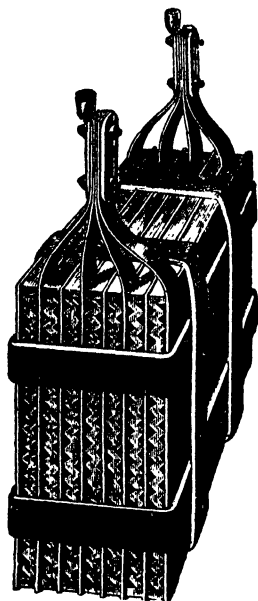


FIG. 45.—Hatch's Electrodes with Zigzag Separators.

each pasted on one side only, were employed for the active materials and then placed together with the grooves on their unpasted sides crossing each other at right angles. By this means a more efficient acid supply is provided for.



FIG. 46.—Usher's Electrode.

In 1892 E. P. Usher described various arrangements for protecting and separating electrodes by means of plates of porous earthenware or kiln-dried wood. His supports were of the type shown in cross-section in Fig. 46, the wide grooves

being filled with active material (in the form of consolidated tablets) and the narrow ones being left free for the electrolyte to circulate through. In 1893 G. H. Roe and G. Sutro also proposed to use porous wood diaphragms for separation and protection, but in this instance the active material was filled into the wood separator, which was grooved to receive it, and flat metal plates were placed against it on either side. Fig. 47 shows the form of separator employed, which is very similar in design to the metallic support of Usher's electrode just described, and also has narrow grooves to hold the free

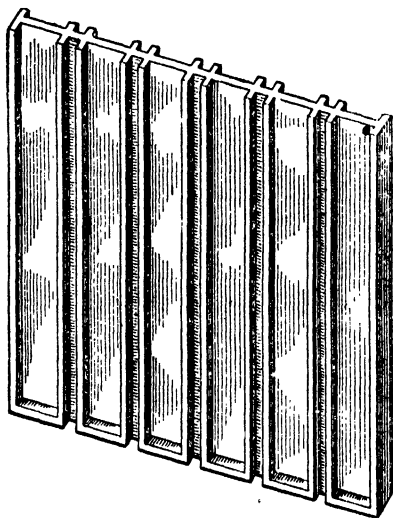


FIG. 47.—Roe and Sutro's Separator.

electrolyte; in fact, the two arrangements are the converse of each other, the one consisting of a grooved support and flat separator, the other a flat support and grooved separator.

Other arrangements in which the electrodes are only separated from each other by porous plates that have to contain the whole, or nearly the whole, of the useful electrolyte, were proposed by G. A. Washburn in 1892 and Menges in 1895, but recognising what an extremely limited amount of acid was thus allowed for, they left hollow channels and ways through the interior of the electrodes so that a further supply could be kept up from the back.

A rather curious method of protection was described in a patent of the Hess Storage Battery Company in 1894. A central cake of active material was held between two metallic grids, whose cells were filled with quartz sand fixed with some binding material. The faces of the grids were covered with some insulating compound to protect them from electrolytic action.

In 1892 S. A. Rosenthal and V. C. Doubleday described a protected electrode consisting of a perforated corrugated sheet lead support pasted with active material and contained in an

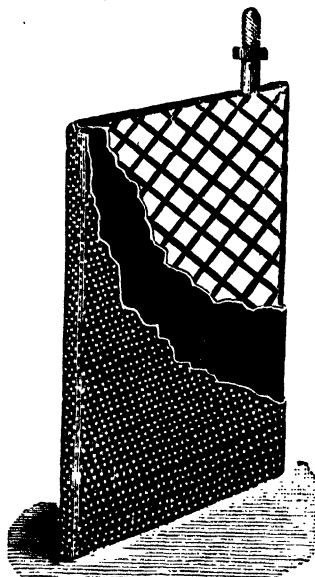


FIG. 48.—Tommasi's Protected Electrode.

ebonite case with perforated sides. In the same year C. Théryc and A. Oblasser patented a form of electrode in which a grid support surrounded with active material was enclosed in a perforated celluloid envelope. Fig. 48 shows a similar electrode designed by D. Tommasi.

In 1894 W. A. B. Buckland patented a support built up of strips of celluloid passed through a slotted lead conducting plate so as to divide it up into a series of parallel chambers on either side, and in 1895 he described a somewhat similar support, but prepared in a different way by sliding perforated

strips of celluloid on to a series of parallel lead rods, and fixing them in position at equal distances apart by flattening out the portions of the rods in between. Fig. 49 gives a side view of this support, and a plan of one of the perforated strips, while a cross-section of a modification in which each of the celluloid shelves has other strips attached to its edges at right angles, in order to provide more support to the active material, is also shown. According to another modification the shelves

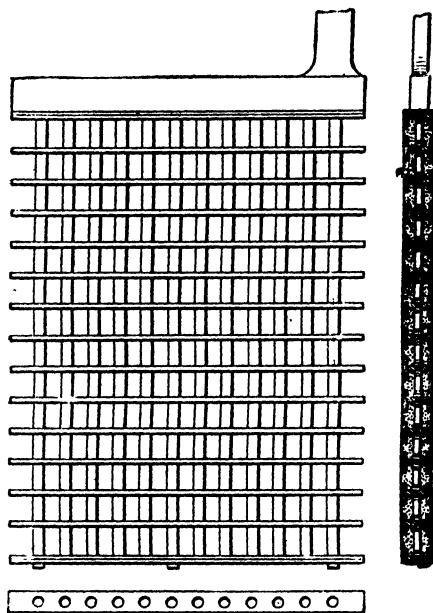


FIG. 49.—Buckland's Electrode.

were held in position by bending or zig-zagging the wires instead of flattening them. After pasting, the electrode was encased in a protective envelope of perforated celluloid, and it then constituted what used to be known as an "I.E.S." plate.

In 1895 Faure after an interval of 14 years again patented a protected form of electrode, this time in conjunction with Frank King. The novelty in this instance did not lie in the arrangement of parts, which was of a very ordinary nature, but in the materials used. The deterioration and ultimate destruction

to which many of the substances usually employed for protective coverings are liable is due not so much to the acid solution in which they are immersed as to the strong oxidising action of the lead peroxide with which they come in contact, and Faure proposed to use a compound protection consisting of an inner layer of silicated asbestos and an outer covering

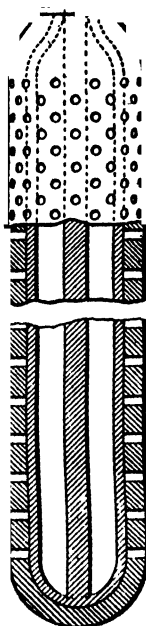


FIG. 50.—Faure's Electrode with Compound Protection.

of perforated celluloid or the like. The former material is prepared by treating asbestos cloth with sodium silicate, and, while itself unaffected by the peroxide, prevents the celluloid which might be acted upon from touching it.

Fig. 50 shows, partly in cross-section and partly in side elevation, the design of electrode illustrated in the patent,

The active material is supported on either side of a central flat conducting plate by sheets—first the porous asbestos fabric, and then the perforated celluloid—bent round the bottom and drawn in and tied at the top.

Later in the year King patented an electrode to which this compound protection or any other could be applied in flat sheets. The support was of the sunk grid type; a shallow grid with raised ridges on either side, which formed a boundary frame and also subdivided it into compartments.

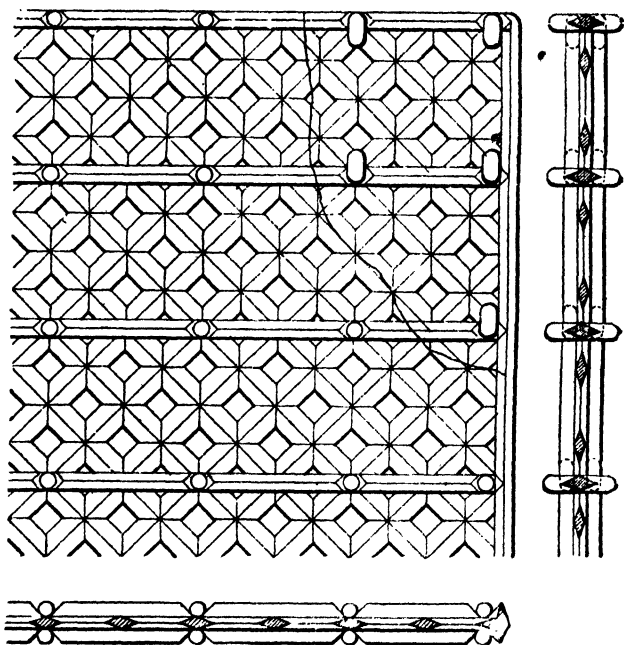


FIG. 51.—Faure-King Grid.

Fig. 51 is a side view and two cross-sections at right angles to each other of a portion of such a support. Pins project from the cross ribs at intervals, and may be bent over, as shown in the right-hand corner of the side view, to hold the protective sheets in position, or else they may be used as guides for grooved separator strips, which are wedged in between the plates and serve the same purpose.

Still later in the year, in another patent, King proposed to use protected electrodes, in which holes or cells are left open at intervals in between the pasted portions, so as to maintain a better supply of acid underneath the protective sheets, and prevent the sulphation of the active material that otherwise is liable to take place.

Fig. 52 gives a side view and cross-section of a support designed on this principle. The round holes *aa* passing right through the electrode from side to side remain unpasted, and serve as reservoirs for the electrolyte. Notches *d* are cut in their edges to facilitate the diffusion of the acid into the

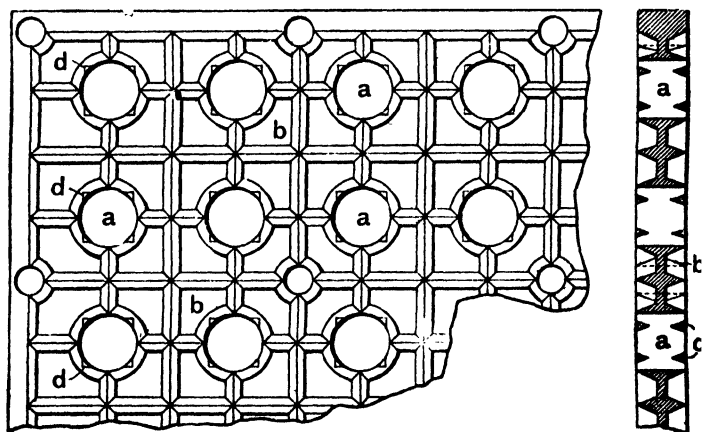


FIG. 52.—Faure-King Grid.

adjacent active material. The portions to be pasted are not open right through, but divided up by a central web or back plate *b*, which converts them into a series of pockets or recesses on either side of the plate.

This series of patents contains some of those which form the basis of the "Faure-King" cell of the Electrical Power Storage Company.

Tubular and Rod Electrodes.

In 1890 H. Woodward proposed to construct electrodes of tubes of perforated india-rubber or other suitable insulating material, containing a central conducting core and active material packed round it. The use of a lead tube underneath

the insulating tube and correspondingly perforated was also mentioned. In the same year Tommasi and Thérȳc patented a very similar electrode, two forms of which are shown in Fig. 53. In both these instances each tube constituted a complete electrode, and the positives and negatives could be grouped and arranged in relation to each other in any desired manner.

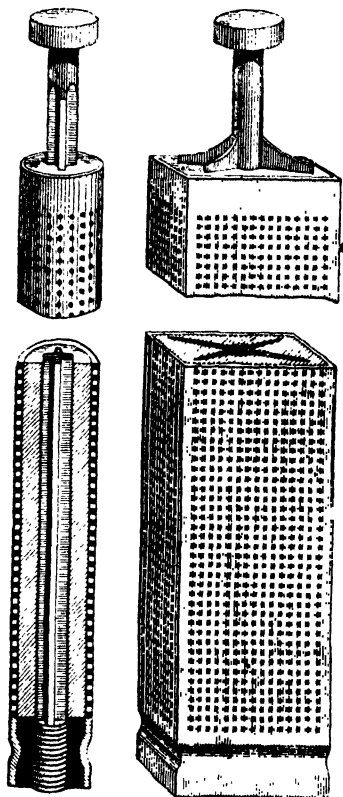


FIG. 53.—Tommasi's Tubular Electrodes.

The more usual procedure, however, with tubular electrodes is to connect a number of them of the same polarity in a row to a main bar, thereby constituting one larger electrode of an approximately rectangular shape. S. Currie patented an electrode of this nature in 1891, in which tubes of woven asbestos

formed the protective covering. The raw active material was lead chloride cast into each tube round a central brass core in the shape of a tapering rod. The core having been withdrawn, molten lead was run in to form the conducting support. Fig. 54 shows an electrode composed of a number of tubes set up side by side and rigidly fixed to main connecting bar top and bottom. In a later modification the asbestos sheaths were drawn direct on to the lead rods, whose surfaces were then converted into lead chloride in an electrolytic bath.

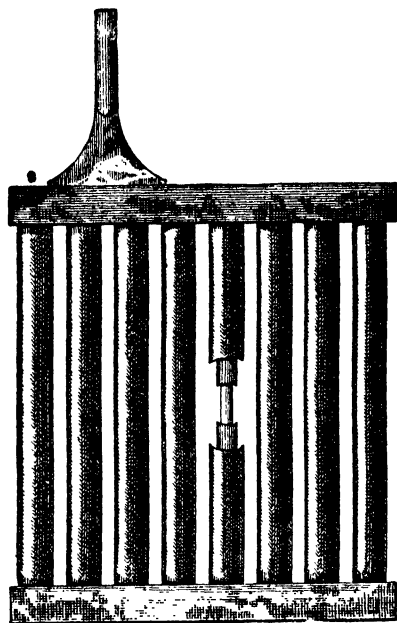


FIG. 54.—Currie's Electrode.

In 1883 E. R. Knowles described some electrodes built up of washers or discs of lead and of lead oxides correspondingly shaped, piled alternately upon each other and clamped together by a lead bolt passing through the central hole. A modification of this construction was to leave the central hole open so as to form hollow electrodes, and to pass two clamping bolts through the holes on either side. According to another modification, a deeply-grooved lead rod constituted the core and support, the oxides being filled into the grooves.

J. B. Lee in 1892 also proposed to use grooved rods, with the object of exposing a series of thin laminæ of metal to the action of the electrolyte, and a spiral grooving was mentioned as being convenient for this purpose. When the grooves were pasted, the laminæ could be bent upwards to form inclined shelves and give a better support to the active material. He further suggested strengthening the rods with central cores of enamelled iron.

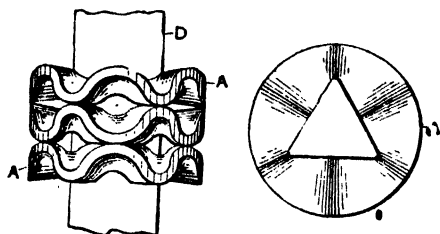


FIG. 55.—Barber-Starkey's Rod Supports.

In 1895 W. J. S. Barber-Starkey patented a variety of rod electrodes, in which washers of various descriptions are strung upon a central conducting core and the active material filled in the interstices between them. Fig. 55 shows a plan of a

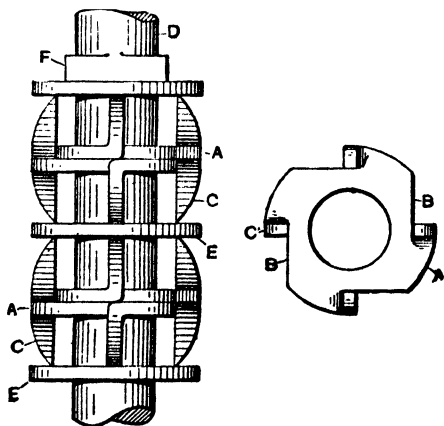


FIG. 56.—Barber-Starkey's Rod Supports.

radially corrugated washer, A, and a view of several of them in position on a rod, D, which is of a triangular cross-section to prevent their shifting round. Fig. 56 shows a

circular washer, A, slit at intervals near the circumference, and the ears, C, thus formed turned up at right angles to form spacing pieces. According to the method of mounting illustrated, these washers are put back to back in pairs with plain ones in between. The principle of the construction shown in Fig. 57 is somewhat different to the other two,

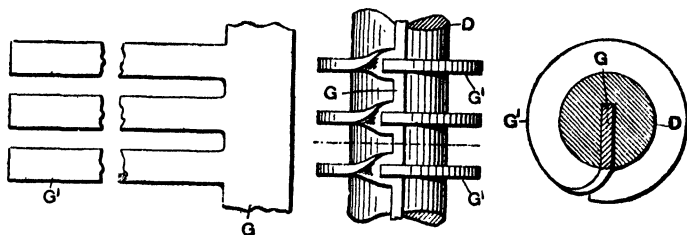


Fig. 57.—Barber-Starkey's Rod Supports.

although the result arrived at is practically the same. The central rod, D, is slotted, and into the slot is inserted the back edge of a strip of lead, G, cut with projecting teeth, G', somewhat like a comb. The teeth are twisted on themselves at right angles and then bent close round the rod.

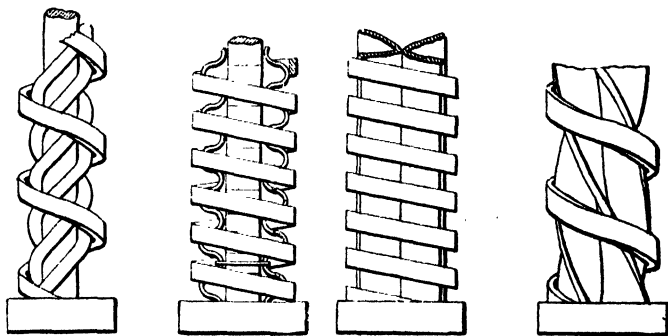


Fig. 58 and Fig. 59.—Vaughan-Sherrin's Rod Supports.

In 1885 H. Thame prepared rod electrodes by winding lead wire spirally on a glass rod and then pasting it flush with the outside of the wire.

Figs. 58 and 59 illustrate the construction of some of the rod supports patented by J. Vaughan-Sherrin in 1896. Those shown in Fig. 58 have a central core, either solid or hollow, of

non-conducting material. Round this core some lead wires are wrapped spirally in the one case, and in the other several crimped strips of lead are attached at intervals by ties of wire to provide the metallic conductors. Upon these again is wound an open spiral of non-conducting strip, and the active material is filled in flush with its outer edge. In the supports shown in Fig. 59 the non-conducting core is dispensed with, and the outer ebonite strip wound direct upon a metallic core such as two L-shaped strips set back to back, or a single strip with four arms, twisted spirally on itself.

In the same year J. D. Brophy and M. M. Andrews also proposed to construct rod electrodes of metallic cores of various cross-sections surrounded with active material, which may be mechanically applied under pressure to the core as it passes through a die of suitable size.

Also, in 1896, Woodward again patented a form of tubular electrode. Lead washers were passed over a central conducting core, and spaced apart by layers of active material in the form of small balls packed between them. The whole is contained in a tube of perforated lead or of insulating material, but the latter is not recommended. Unlike most electrodes of this type, it does not appear to be intended for mounting in rows on a main bar, but to be used as a central electrode surrounded by a number of smaller ones of opposite polarity.

Thin Sheet and Strip Supports.

To produce electrodes containing a high percentage weight of active material, supports have frequently been proposed in which some arrangement of sheet lead is substituted for the heavier cast grid or grooved plates.

In 1881 Sellon, in one of his patents, illustrated two arrangements of perforated sheet for supports, one dovetailed and the other corrugated or pleated (*see* Fig. 60). Brush mentioned the use of corrugated sheet in one of his earliest patents, filed in 1881, and he illustrated a sheet corrugated in two directions at right angles to each other, as shown in Fig. 61. In 1886 E. M. Gardner constructed supports by dividing the central portion of a sheet of lead into a series of parallel sections, leaving each one attached to the body of the sheet by a small strip at either end; then he twisted these sections at right angles

to the plane of the sheet, and bent up their edges so as to form a series of curved troughs or trays. Fig. 62 is a plan of a portion of one of these sheets, showing the upper part twisted and bent up into trays and the lower part cut ready for twisting. In the cross-section the whole of the trays are bent and finished. In the same year W. Taylor described supports of lead



FIG. 62.—Sellon's Corrugated Sheet Supports.

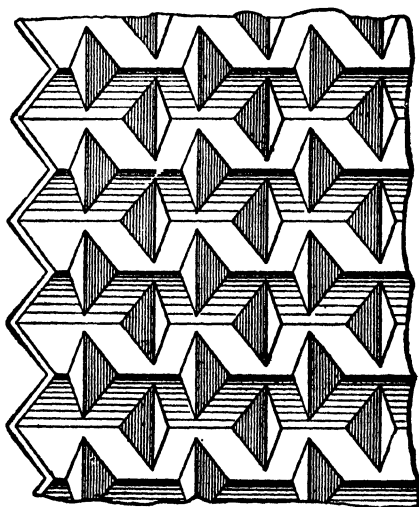


FIG. 61.—Brush's Corrugated Sheet Support.

strips, corrugated both longitudinally and transversely, spaced some distance apart and cast in a frame. He also mentioned that his lead strip may be produced by "squirting" under pressure.

Also, in 1886, C. Sorley introduced a support consisting of interwoven horizontal and vertical strips, and in 1889 he

constructed another form of strip electrode, shown in Fig. 63 ; while in 1890 T. Ewing patented a support of a very similar nature.

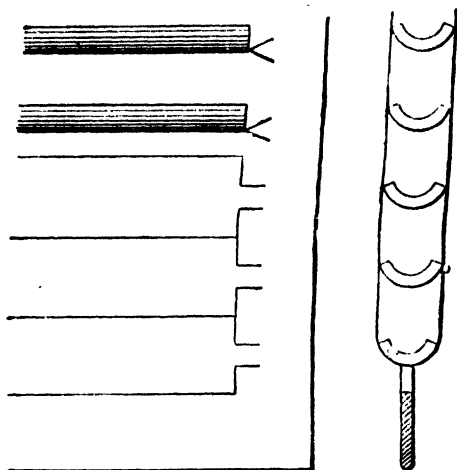


FIG. 62.—Gardner's Support.

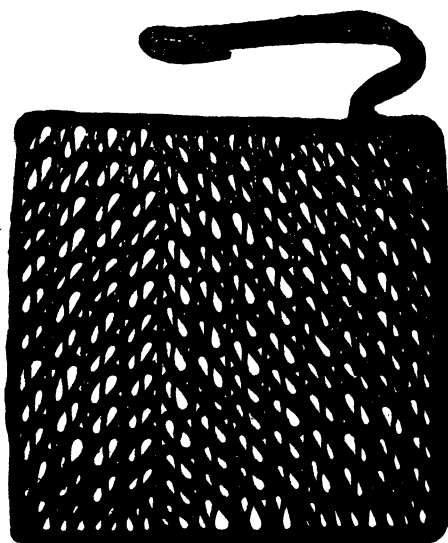


FIG. 63.—Sorley's Strip Electrode.

In 1887 H. Mower prepared supports from thin strips twisted up spirally and cast on to a main bar in rows. This device has often been employed since, and Fig. 64 shows its use in one of Usher's supports described in 1893. In this

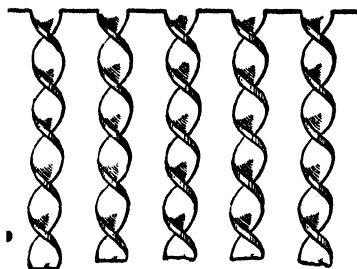


FIG. 64.—Usher's Twisted Strip Support.

case, however, instead of twisting up a number of independent strips and uniting them afterwards, they are all prepared from one sheet suitably slit up.

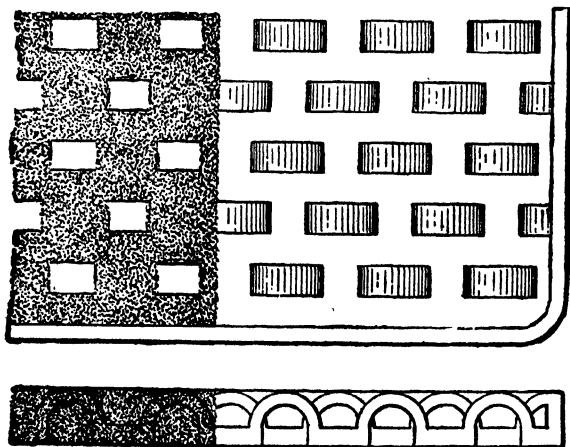


FIG. 65.—Gibson's Support.

A form of support patented by the Gibson Electric Company in 1889 is shown in Fig. 65. It consisted of a flat sheet of lead, out of which raised semi-circular loops are pressed so as to provide keying pieces for the active material. In the same

year H. T. Cheswright described the use of a perforated sheet, in which the holes were pushed, not punched, out, so that the displaced metal stood up in a jagged rim all round them, as shown in Fig. 66, and helped to hold the active material in position. *This idea has also been utilised by many others.*

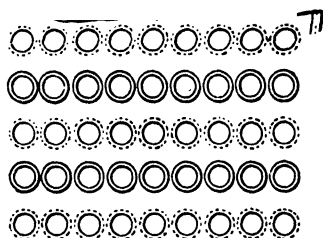


FIG. 66.—Cheswright's Support.

The revived use of protected electrodes has led to the introduction of a good many thin sheet supports within recent years, but none of them of any great novelty of design. A combination of perforated sheet, either flat or corrugated, was patented by J. T. Niblett in 1891; and corrugated sheet was

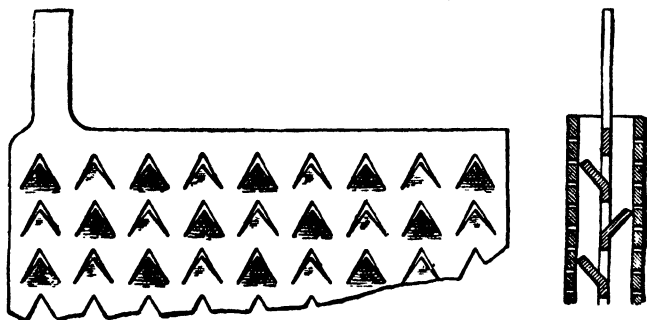


FIG. 67.—McDougall's Support.

also employed by Rosenthal and Doubleday in 1892, and by O. March and by A. Schanschieff in 1894. Another modification employed by M. Sussmann in 1893 was to cut a series of triangular or rectangular notches all over a thin sheet and then push them out alternately on either side. Fig. 67

shows a portion of a plate of this nature proposed by W. M. McDougall in 1895.

Still more recent are the supports patented by L. Guelzow in 1897 and by W. A. Crowds in 1898. In the former the thin sheet has long rectangular strips notched out and bent in either direction, as shown in Fig. 68, while the latter has nearly half the metal removed by stamping, so as to leave the

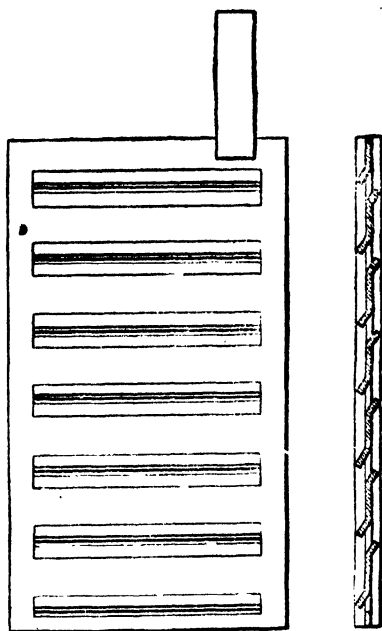


FIG. 68.—Guelzow's Support.

sheet covered with rows of oblong perforations, and the bars in between these are then bent right and left as shown in Fig. 69.

In practice most electrodes containing thin metal supports require to be further strengthened mechanically. Although not always specifically stated, many have a stiff frame of lead cast round them to give rigidity; or, if this is dispensed with, some form of "protection" which fulfils the same purpose is employed.

A third method is to provide frames or grids of some non-metallic material such as celluloid or ebonite, which both stiffen the support and at the same time help to carry the active material. Sellon patented the use of two non-conducting grids clamped on either side of a central conducting sheet in 1881, and this construction appears to have been a favourite one with inventors, for it has been proposed with various slight modifications several times since. Maxwell Lyte described it in 1883, W. P. Kookogey in 1889, and in 1891 P. Kennedy

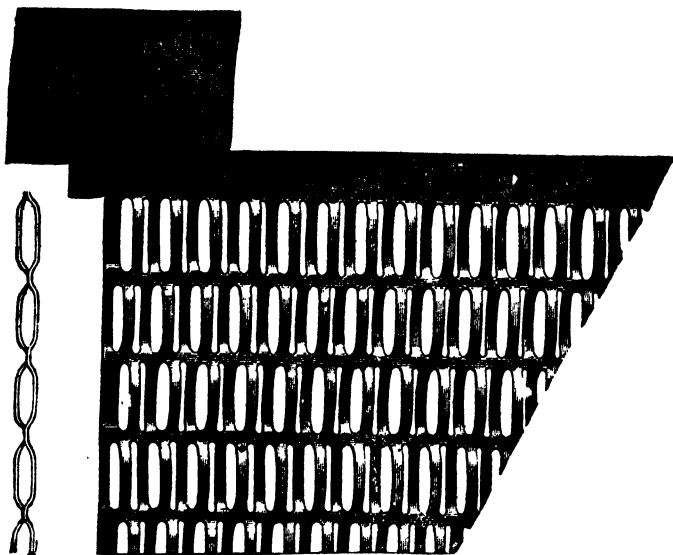


FIG. 69.—Crowdus' Support.

proposed to use a slotted central conductor and to have projections on the inner sides of the grids which should meet through the slots and be united by heating and pressure. In Guelzow's electrode, the support, just previously illustrated (see Fig. 68) was strengthened by clamping its edges between two thin frames of ebonite.

In 1885 and 1886 Jones and Tasker described a variety of supports in which non-conducting substances were freely used. In many of these arrangements, however, they merely served as carriers for strips of gold, platinum, &c., which formed the

conductors in electrodes of the solid peroxide or "lithanode" type. In others, thin sheet or strips or wires were partially embedded in frames of celluloid or were interwoven with celluloid strips.

In 1895 J. J. Rooney patented a grid support built up in layers of strips of wool-felt and having strips of thin corrugated lead embedded in its centre for conductive purposes. The whole is cemented together and consolidated by combined heat and pressure.

Wire Supports.

These supports offer the same general characteristics as the thin sheet and strip supports just described. The favourite construction has always been to plait or weave the wires into some form of gauze or net, as this gives them a stability which they do not individually possess. It also allows the support to be very intimately distributed through the active material, and there is not therefore so much occasion for the use of protection to hold them together; but a stiff surrounding frame of some kind is generally required.

In 1881 Faure proposed to construct electrodes of a cable of wires folded backwards and forwards on itself to form flat plates, the active material being contained in the interstices between the wires. FitzGerald, C. H. W. Biggs, and Beaumont described the use of lead wire gauze as a basis on which to deposit spongy lead, a number of such layers being consolidated by pressure to form an electrode. Almost identical methods were also proposed by A. K. Eaton, by A. Khotinsky, and by N. De Kabath shortly afterwards.

In 1882 F. W. Durham and P. Ward patented the use of wire of a similar cross-section to that of the pinion wire used by watchmakers, and proposed to wind it either in flat spirals or lengthways or crossways, or both combined, upon a flat back-plate; and L. H. M. Somzée also described various arrangements of open work wire netting to contain the active material. In the same year Brush proposed to use a wire of some unoxidisable alloy of lead for supports either woven into a gauze or in some other manner.

In 1883 E. T. Starr described various arrangements of woven wires contained in a rigid surrounding frame, one of

these being to superimpose several layers of wire gauze either in close contact or with a small space between each.

M. Bailey and J. Warner patented some gauze electrodes in 1887, and in the following year they proposed to interweave the lead wires with threads of twine, silica, asbestos fibre, &c., in order to allow more room for expansion and active material.

In 1890 J. and L. Legay built up electrodes by winding a cable of wires longitudinally on a frame, or else by cutting the cable into a number of equal lengths, which were placed side by side and burned into a main connecting bar.

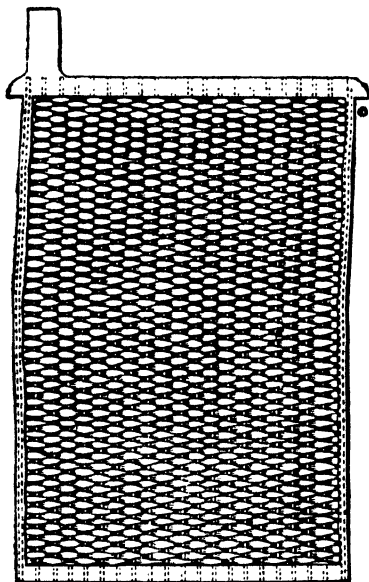


FIG. 70.—Gülcher's Electrode.

In 1889 J. B. Entz and W. A. Phillips patented a compound wire, consisting of a braiding or network of fine wires woven round a larger central wire. The active material was to be packed in the interstices between the fine wires, and the compound wire could be made up into electrodes in any desired manner and form. This method of construction was specially intended to be carried out in copper wire with a filling of

copper oxide, for use as the positive electrode in alkaline cells, but it is equally applicable to other metals, such as lead.

One of the latest applications of wire to pasted supports is that patented by R. J. Gülcher in 1896, and consisting of a woven fabric having lead wires as warp and bundles of fine fibres or filaments of glass, quartz, &c., as weft. As usual, there is a stout metal frame cast all round it. This electrode is illustrated in Fig. 70.

Metallic Envelope Electrodes.

These electrodes are also closely allied to the two preceding classes. Sometimes they contain a central metallic support, but more generally the entire current is collected and distributed by the exterior envelope of sheet metal. Faure in 1881 and Somzée in 1882 proposed to hold the active material

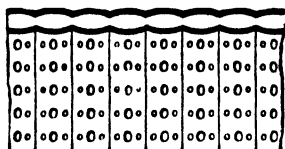


FIG. 71.—Sellon's Envelope Support.

against the central support by covering it with lead wire gauze, thereby forming a kind of metallic envelope, and this method has since been employed by others; but the first true envelope electrode appears to have been proposed by Sellon in 1881, when he described what he called a "compound plate," consisting of two perforated sheets of lead with active material filled in between them. The sheets were held apart by rivets, or a frame or bars could be attached to their edges so as to form a hollow receptacle enclosed at the sides. The sheets themselves could be flat, corrugated, or waved. The latter form is shown in Fig. 71. Volckmar, in France, illustrated a perforated envelope type of support in one of his patents of the same year. Starr also appears to have worked at electrodes of somewhat similar construction, his results being embodied in United States patents from 1881 to 1884. When perforating the lead sheets he did not stamp the metal out, but simply pushed it inwards to form a series of projecting burrs and

thereby give a better hold on the active material. Fig. 72 shows a portion of such a case in cross-section. This construction was also employed by A. Stetson in 1887, and the same device for producing burrs round the perforations has been used many times since.



FIG. 72.—Starr's Envelope Support.

Other early forms of envelope electrodes were De Kabath's, packed with spongy lead or with lead strips; Simmen's, with tangled masses of threads or wires (*see* Fig. 73); and Somzée's, with strips of pasted gauze or perforated sheet.

In 1887 Epstein proposed to construct electrodes by casting a lead sheet round cakes of active material, and then cutting slots or holes through this outer envelope; and H. H. Carpenter prepared electrodes in a similar manner in 1889, per-

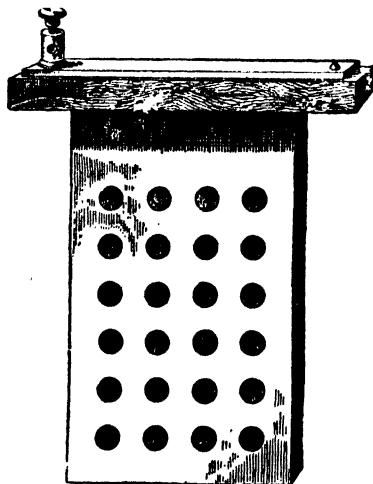


FIG. 73.—Simmen's Envelope Electrode.

forating the plates from side to side through both the envelope and the active material. In the same year Knowles enclosed cakes of active material between two slight perforated plates of cast metal, which were held together by rivets at intervals and also by the edges of the one plate being turned down over

those of the other. Fig. 74 gives a plan and cross-section of this electrode. Also in 1889 C. H. Logan described various forms of envelope supports which he preferred to slot rather than perforate, as he considered that it afforded a better allowance for expansion.

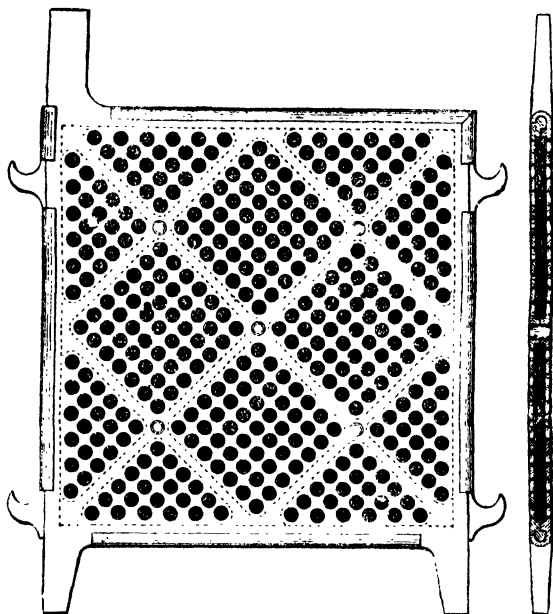


FIG. 74.—Knowles' Electrode.

In 1890 G. A. Johnson prepared envelope supports by folding a sheet of corrugated perforated metal double on itself, attaching the opposite ends to a main bar, and closing the sides, after filling with active material, by doubling one sheet

FIG. 75.—Johnson's Envelope Support.

over the other; or two separate sheets might be used (*see* Fig. 75), and closed all round in this way. A little later, in conjunction with S. L. Holdrege, he modified this construction, and used a pair of shallow trays of perforated lead for his envelopes, the trays being ribbed at intervals to divide the

active material up into sections. A somewhat similar arrangement of pairs of flanged trays bolted together was introduced by C. W. Kennedy and H. Groswith at about the same time.

In 1892 W. W. Donaldson and R. Macrae also patented an electrode, in which the active material was contained in a

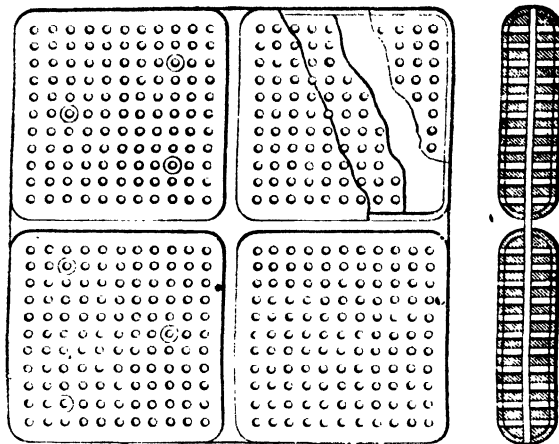


FIG. 76.—Donaldson and Macrae's Electrode.

air of shallow trays of perforated lead, burned together around their edges. For larger plates a number of such compartments were held together by a frame or grid cast round them, or, as an alternative method, instead of joining the compartments directly together, they could be burned on opposite sides of a central lead plate of sufficient size to take any required number of them. This arrangement is illustrated in Fig. 76.

Still another support, consisting of a pair of shallow perforated trays burned together, is that of C. J. Barbier, patented



FIG. 77.—Barbier's Envelope Support.

in 1893, the speciality in this instance being the pins projecting from the inner surfaces of the trays into the body of the active material to give a more equal distribution of the current to all parts of it. Fig. 77 shows a portion of such an electrode, partly in side elevation and partly in cross-section.

Volckmar or "Plugged" Electrodes.

The feature common to all electrodes of this class is their metallic packing, consisting of portions of lead which are quite independent from the support proper and not in true connection with it. This packing has to be electro-chemically "formed" just as an ordinary Planté plate to give the electrode any storage capacity, and for this purpose it is arranged so as to offer a large exposed surface within a small space. It is in the form and disposition of the plugs or packing that the chief difference between the various electrodes of this type lies, for the support is generally a large-holed grid or other simple form of frame possessing no very distinctive features.

The origin of these electrodes followed closely on Faure's discovery of the large capacity to be obtained by the use of applied active material, and appears to have been largely due to an endeavour to obtain equivalent results without infringing his patents. In 1881, at about the same time that Swan and Sellon patented their cellular grids and thin sheet supports in England, Volckmar also patented substantially the same devices in France; but he only proposed to fill the cells or receptacles of his supports with metallic lead either in the form of powder, dust, granules, filings, threads, wires or foil, or else in a chemically subdivided or spongy state. The latter form of the metal differs from all the others, in that it is fully prepared active material ready for use, and it is doubtful therefore whether it did not come within Faure's claims; but the ultimate combination effected between the Faure, Sellon, and Volckmar interests obviated the necessity that might otherwise have arisen for close inquiry into this or similar points.

In the same year Tommasi described a form of electrode, in which the support consisted of a rectangular frame of lead divided up by a number of horizontal shelves (*see* Fig. 78) Apparently he only contemplated using two such electrodes in a cell, for, as shown in the illustration, they were closed in at the back and the shelves sloped upwards towards the open face. The long, narrow pockets thus formed between the shelves were packed with layers of lead foil about $\frac{1}{350}$ th of an inch thick or even thinner.

A third electrode of 1881, also belonging to the class under consideration, was De Kabath's well-known form, composed

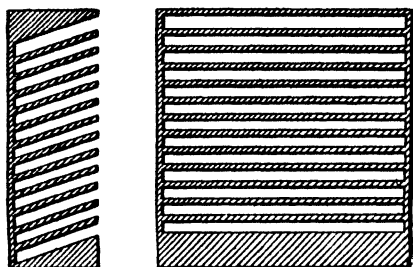


FIG. 78.—Tommasi's Electrode.

of a number of strips of lead $\frac{1}{16}$ th of an inch thick, packed side by side, and enclosed in a perforated lead case or support. The strips were alternately flat and corrugated in order to

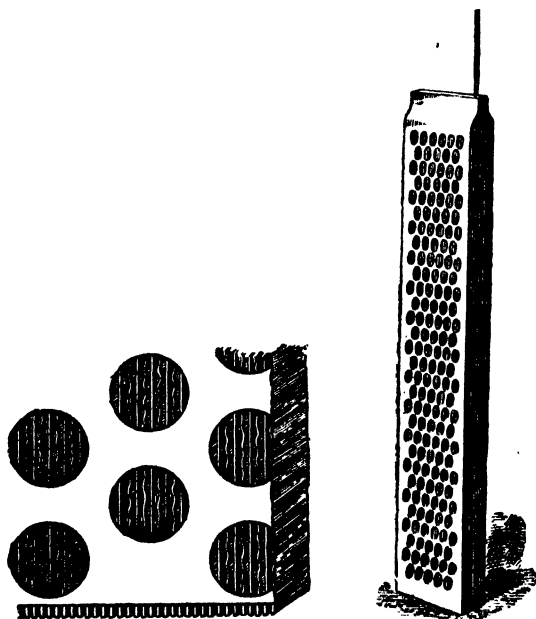


FIG. 79.—De Kabath's Electrode.

keep their surfaces apart and expose as much of them as possible to the action of the electrolyte. Fig. 79 shows one of

these electrodes, also a portion of the same on an enlarged scale.

It is usual to treat these electrodes of Tommasi and DeKabath as being modifications and improvements upon Planté's original plates, but seeing that the lead foil employed was so exceedingly thin, that it was not in any way directly attached to its support, and that nitric acid was used to hasten its oxidisation, it would appear that the object was rather to convert the whole of the foil into masses of active material and thereby produce electrodes possessing all the characteristics of Faure's rather than of Planté's method of construction. This, at any rate, would be the ultimate result, whether desired or not, provided that the supporting frames or cases, which were themselves of a very slight nature, were not first destroyed.

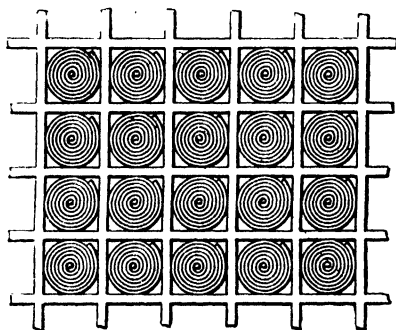


FIG. 80.—Elieson's Plugged Electrode.

In 1885 C. P. Elieson patented a grid electrode, in which every hole or cell was plugged with a round pellet made up of a strip of lead and a strip of asbestos cloth rolled up spirally together, the object of the asbestos being to keep the layers of lead apart and allow for access of the electrolyte and growth of active material. Fig. 80 shows a portion of such an electrode with square cells in the grid, but they could be of other shapes if desired.

In the following year C. Smith also proposed to fill a grid support with alternate strips of lead foil and asbestos, but instead of rolling into a spiral he packed a number of them

alongside to form rectangular blocks which were then forced into the holes in the grid under pressure. Fig. 81 illustrates a portion of his electrode. An alternative method of construction was to coat the lead strips with lead peroxide in place of the asbestos strips, and to put their ends in direct metallic connection with the frame. In 1892 W. W. Griscom described an electrode somewhat similar to that of Smith, but in this instance the strips of lead foil were spaced a small distance apart without any separating material between them, and the grid frame cast direct on to their ends. Although the strips are at first in direct contact with the support, it is specially mentioned that they shall be thin enough to be

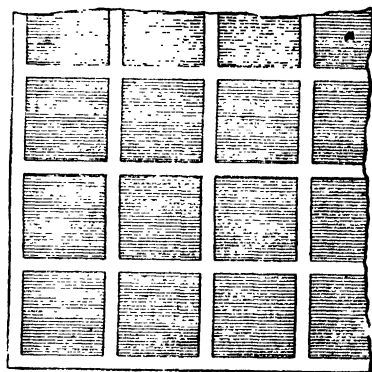


FIG. 81.—Smith's Electrode.

rapidly eaten through during the working of the cell, and so finally converted into active material with shreds of detached metallic lead left scattered here and there in its midst.

In a form of electrode patented by Gibson in 1888 a double-headed stud of lead was jammed into each hole of a grid support, and then the remainder of the space between the stud and the frame filled in with active material (*see* Fig. 82).

Strictly speaking, this plate belongs to the pasted grid type, as the purpose of the studs is chiefly to afford better support for the active material, but the device of plugging the holes with independent pieces of metal suggests a certain similarity to those now being described.

In 1891 J. H. Walter proposed to plug a round-holed grid with spirals made up of strips of lead, crimped or corru-

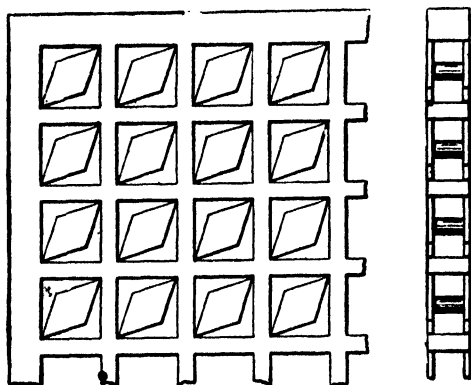


FIG. 82.—Gibson's Studded Grid.

gated to give them a rough or irregular surface (*see* Fig. 88), and in 1894 C. J. Hall described the use of strips with smooth

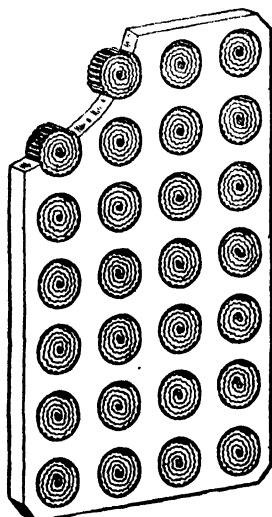


FIG. 83.—Walter's Electrode.

surfaces in a similar way, burring over the edges of the holes to keep the spirals in position in the frame.

A still more recent patent for electrodes of this class is that of J. G. A. Rhodin in 1895, which is the basis both of the "R"



FIG. 84.—Rhodin's Plug.

type positive plate manufactured by the Chloride Electrical Storage Syndicate in this country and of the "Manchester" type

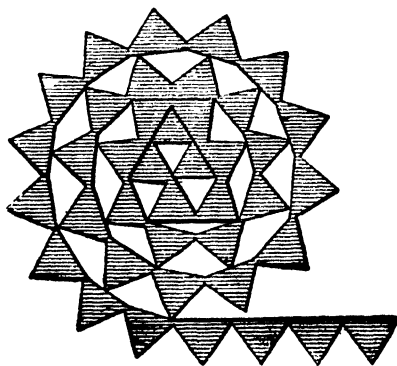
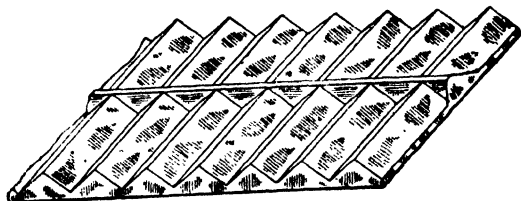


FIG. 85.—Grindle's Plug.

plate manufactured by the Electric Storage Battery Company in the United States. The object he aimed at was to plug the

holes in a grid with bundles of separate wires, as proposed by Volckmar, but in order to carry this out in a practical and commercial way, sheets or strips of lead were pressed to form the equivalent to a number of wires joined by thin bands or fins of metal. Fig. 84 shows a portion of a strip of triangular wires, the shape used in practice, and two cross-sections of alternative shapes, the one round and the other rectangular. The fins of metal connecting the wires were to be thin enough to be soon eaten through by the formation and subsequent local action during working, leaving practically detached wires surrounded by oxides in each hole, but this feature is modified in a patent of R. J. W. Grindle's in 1896, according to which the whole of the wires are united, in addition to the fins, by a central transverse rib as substantial as the wires themselves. Fig. 85 shows on an enlarged scale a portion of this modified form of strip, and also a side view of a rolled-up spiral, the latter equally illustrating either the earlier or more recent construction.

Planté or "Formed" Electrodes.

All supports of the Planté type are designed with a view to affording as large a surface as possible from which active material can be electrolytically prepared. Some kinds of supports are naturally more suited for use with one type of electrode than the other, and just as grids are almost entirely confined to pasted electrodes, so grooved and ribbed plates are mostly associated with those of the formed type. There are other supports, however, such as those composed of thin sheet or strip, which may, by a different arrangement of parts, be equally well adapted to either type of electrode; and these are here split up into two classes, according to the purpose for which they are primarily intended. Those for pasted electrodes have already been described, and the remainder will now be dealt with.

Grooved or Ribbed Supports.

Brush, in a United States patent filed in June, 1881, appears to have been the first to propose a perforated, ribbed, or slotted support, specifically designed for electro-chemical formation but in a second patent, filed one week later, he described and

illustrated exactly the same supports for pasted electrodes. Fig. 86 gives some of the grooved varieties.

Swan's ribbed support, shown in Fig. 87, was patented earlier than Brush's, but also seems to have been intended for the reception of applied active material. In a second patent

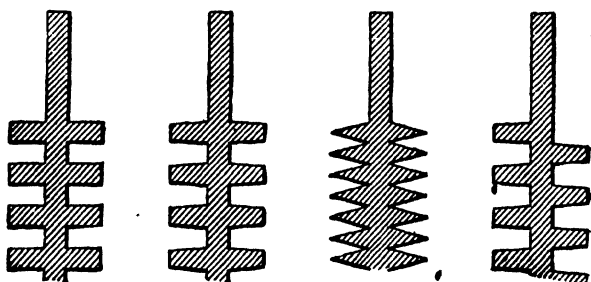


FIG. 86.—Brush's Ribbed Plates.

of 1881, however, Swan described a support to be electrochemically formed, and having its surfaces divided up into a series of ribs or grooves so minute as to produce the effect of a fine mat or pile of lead. This result could be obtained

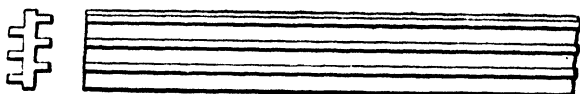


FIG. 87.—Swan's Ribbed Plate.

either by scraping smooth surfaces with a cutting tool, or by pressure between engraved plates, but in any case solid strips or ribs were to be left at intervals between the laminated portions, to maintain the strength of the electrode.



FIG. 88.—Brush's Saw Tooth Plate.

In one of Brush's United States patents of 1882 a support is mentioned whose ribs in cross-section resemble the teeth of a saw (see Fig. 88), and Hochhausen also illustrated a similar construction in 1888. Both of these were intended for pasted

electrodes, but in 1882 Sorley patented a support of the same nature for electro-chemical formation.

In Germany grooved supports were employed by Tudor at an early date, and they have been used ever since for the well-known electrodes associated with his name and manufactured by the Accumulatorenfabrik Actien-Gesellschaft of Hagen in Westphalia, for which reason they are often designated as the "A.-F.-A.-G." plates. Commencing with an ordinary pasted positive and then passing to one in which the paste was only relied on to supply an initial and temporary output until such time as the surfaces underneath were sufficiently peroxidised,

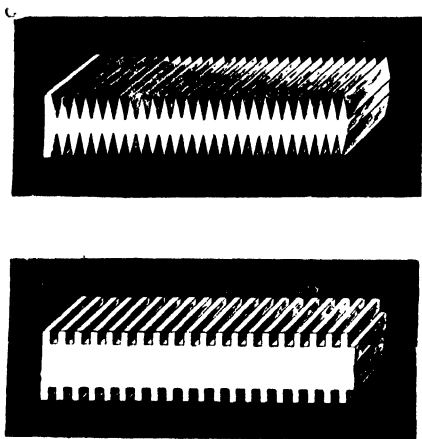


FIG. 89.—Tudor Plates.

they soon discarded both these kinds in favour of a true Planté electrode containing no applied active material whatever, but for the negatives pasted plates have been used throughout. Various modifications have also been made from time to time in the mechanical design of the electrodes.

Fig. 89, shows portions of two early types of positive used before the art of casting their plates with deep grooves and fine ribs had been brought to the state of perfection it has since attained.

In 1891 Tudor proposed to increase the exposed surface of the supports by running a series of fine grooves at right angles across the deeper grooves, which were now by preference placed

vertically. A modification of this arrangement was to build up the electrode of a number of bars covered with a series of grooves at right angles to their length, the bars being fixed vertically and parallel to each other in a surrounding frame. Fig. 90 shows in elevation and cross-section a portion of such

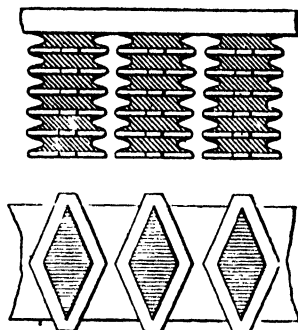


FIG. 90.—Tudor's Grooved Rod Support.

an electrode constructed of diamond section bars, and it will be perceived that the juxtaposition of the bars produces the effect of the larger vertical grooves, except that they pass

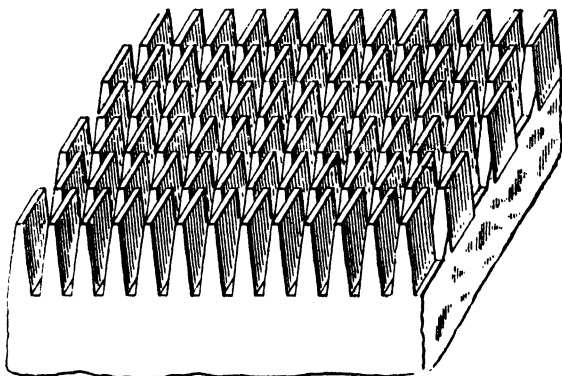


FIG. 91.—Müller's Studded Plate.

right through from side to side instead of being divided by a central partition. A. Müller in 1892 described another method of obtaining increased exposed surface by doing away with alternate sections of adjacent grooves so as to leave rows of projections and intervening spaces, as shown in Fig. 91.

In 1890-91 Cheswright patented supports with vertically grooved faces, the speciality being their hollow construction either in the form of a number of tubes placed alongside, or as a hollow rectangular plate strengthened internally with cross-partitions.

In practice most grooved supports are strengthened by ribs running across the grooves at intervals and dividing them up into a series of oblong cells or pockets. In 1892 Heyl proposed to slot these bars from end to end and so allow for expansion of the active material in the grooves, this being substantially the same as his method, already described and illustrated on page 28, of providing for a similar growth of grid supports.

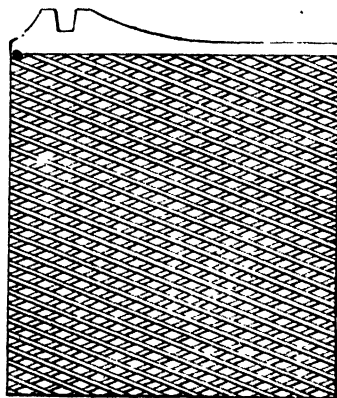


FIG. 92.—Harris and Holland's Electrode.

In 1896 G. W. Harris and R. J. Holland obtained a United States patent for an electrode in which the grooves on either side of the plate were situated at an angle to each other with a view to the more equal distribution of the strain experienced by the support during its formation. But with this construction it was possible to dispense with the central metallic core altogether, simply leaving the ribs in direct contact at the points where they crossed each other and producing a kind of double grid or lattice-work plate as shown in Fig. 92. It will be observed that the lattice is not surrounded by the usual solid rim or frame. This is purposely omitted, so that the allowance for expansion may be as complete as possible.

In 1897 R. R. Berks and J. Renger described supports having zigzag or corrugated ribs for the purpose of obtaining a better hold on the active material. Fig. 93 gives cross-sections of two designs of this nature, the one with the ribs close together being intended for a Planté-formed positive, and the other for a pasted negative.

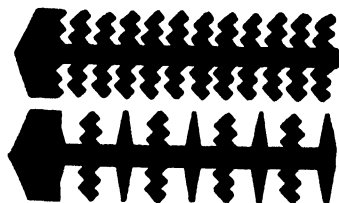


FIG. 93.—Berks and Renger's Plates.

Many other grooved electrodes have been proposed and employed at various times, but as they do not embody any novel features of design, they hardly call for special description here. Those more especially intended for Faure type electrodes have already been referred to under "recessed and pocket supports."

Thin Sheet Electrodes.

Planté's own electrodes were the first of this type. His original form, described in 1860, consisted of two long sheets of thin lead rolled up into a close spiral, with a layer of flannel between. His plate electrodes consisted simply of single sheets of flat unperforated lead. De Kabath in 1881 proposed to wind several thin sheets one upon the other round a thicker central plate, and also to corrugate the sheets; but he does not appear to have then made any provision for overcoming the screening effect that must necessarily be exerted by the outside sheet. In 1883, however, he modified this construction by making U or V-shaped cuts at intervals all over the sheets, and then rolled back the tongues thus formed to serve as spacing-pieces between the different layers, and to leave openings for the penetration of the electrolytic action to those innermost. Fig. 94 shows a portion of one of these sheets in elevation, and two cross-sections at right angles to each other.

Another patent of 1881 for sheet electrodes was that of Fitzgerald, Biggs, and Beaumont. They minutely punctured thin sheets of lead by means of bundles of needles held in a reciprocating tool, and then united a number of them together by pressure, after first superficially sulphating their surfaces to prevent too complete adhesion.

In 1887 W. Main proposed an electrode constructed on somewhat the same lines. A number of thin sheets were riveted together to form a compound plate, and the whole mass then perforated transversely. The individual sheets could also be perforated before building up, and by having their surfaces roughened he considered sufficient space would be allowed between the sheets for the active material and penetration of the electrolyte.

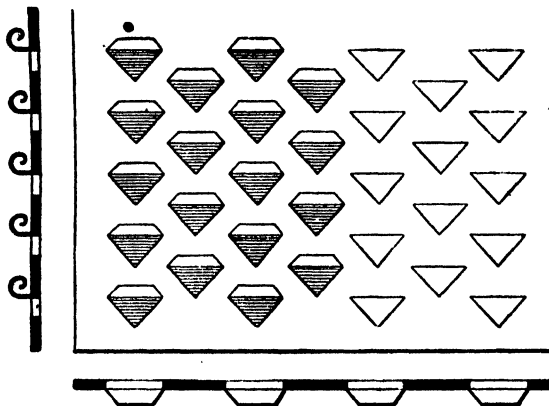


FIG. 94.—De Kabath's Perforated Sheet Support.

In 1891 Elieson patented electrodes consisting of sheets of perforated corrugated lead wrapped one over the other; the corrugations running at right angles in adjacent sheets so as to keep their surfaces properly spaced apart. A feature of his earlier electrodes of this kind was their construction in the form of hollow cylinders or rectangles, but he afterwards conformed to the more usual practice and adapted the flat-plate type.

Crimped or Pleated Sheet Electrodes.

By pleating sheets into a series of narrow folds, concertina-fashion, instead of superimposing a number of layers, electrodes

may be obtained which offer an equally large exposed surface for the same thickness, but without any screening effect being exerted between their various parts; and other advantages also result from this modification.

Both A. De Meritens and Brush constructed electrodes of this kind in 1881, but they are more closely identified with E. Reynier, who designed various forms on the same principle in 1888 and the following years, and studied their behaviour very thoroughly. In one of them, a sheet of lead was folded twice

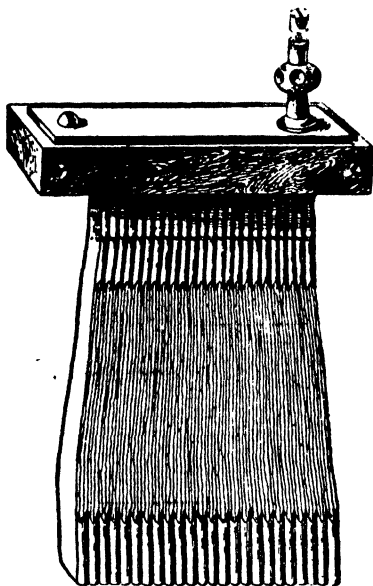


FIG. 95.—Reynier's Pleated Sheet Electrode.

upon itself to form three layers, and then pleated. The longitudinal edges of the outer sheets were split open nearly from top to bottom, in order to give access to both their sides and to the inner sheet, and finally the pleated block was attached to a main bar at one end. The formation of active material pushed the folds of the pleats somewhat apart at their free ends, causing the electrode to assume the appearance of a fan, as shown in Fig. 95, and to overcome this trouble the pleated sheet was enclosed by a metal frame on all sides. Even this

arrangement could not control the expansion, which exerted sufficient force to bulge out the sides of the frame; so, finally, a lozenge-shaped piece had to be cut out of the centre of the

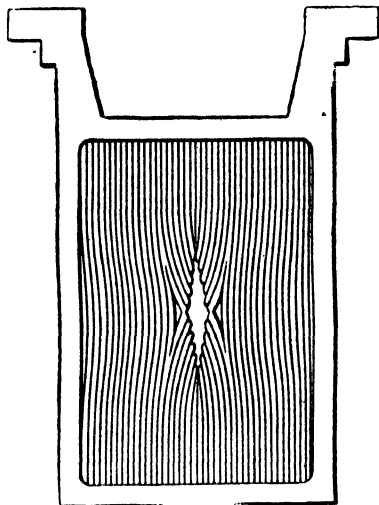


FIG 96.—Reynier's Pleated Sheet Electrode (before formation).

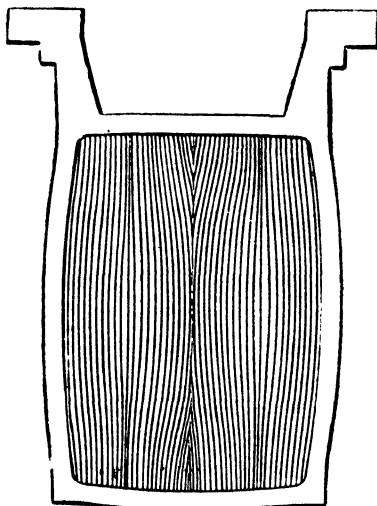


FIG 97.—Reynier's Pleated Sheet Electrode (after formation).

electrode (or rather out of the centre of the sheet before pleating), so that the expansion could be taken up internally and the strain on the frame relieved. Figs. 96 and 97 illustrate this electrode before and after formation.

A form of pleated sheet electrode was patented by I. A. Timmis in 1894, but in this instance the sheet was first obliquely corrugated in order to keep the surfaces of adjacent folds of the pleats apart. In this way strips of sheet a few inches wide were made up into blocks the thickness of the required electrode, and then attached by one edge to a main connecting bar. This bar is situated vertically in the centre of the electrode, and has a block or series of blocks on either side of it, whose other ends are left free to allow for growth and expansion.

Strip Electrodes.

Strip or ribbon supports have been used very frequently for Planté electrodes. The strips are mostly arranged either vertically, horizontally, or in flat spirals or spools.

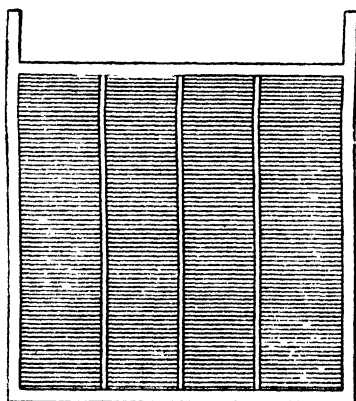


FIG. 98.—Tommasi's Strip Electrode

Tommasi in 1881 described an electrode of the first kind, which is typical of numerous later varieties. A number of strips of lead foil were piled one upon the other, and then burned into a surrounding frame, their ends being turned in on themselves to provide spacing pieces between adjacent strips. Fig. 98 is a front view of this electrode with

strengthening bars, to which the strips are also burned, crossing the plate vertically at intervals. In 1882 J. J. Barrier and F. T. Vernède proposed to keep the strips apart with layers of platinised carbon, and in the same year St. G. Lane-Fox suggested the use of layers of sand, asbestos paper, or other porous non-conducting material, while in 1887 W. H. Akester employed horsehair for the same purpose. In all these electrodes the enclosing frame rigidly held both ends of the strips, and prevented their elongation when peroxidised, so that their inevitable and natural growth had to be taken up in the body of the plate, and tended to cause distortion and buckling. For this reason the complete frame was dispensed with in many electrodes, and the strips merely united together at one or both ends. In 1884 E. Jones constructed plates of piles of strips of a somewhat oval section, similar to that of a double convex lens, joining one end of a number of these piles into a vertical connecting plate, but leaving their other ends quite free. The strips rested in direct contact along the central plane of the plate, but, owing to their section, gradually opened further apart towards either surface.

In the same year J. S. Beeman proposed to divide up solid plates into horizontal strips by a series of parallel cross-cuts with a saw, leaving sufficient uncut metal at one edge to hold them together and form a main conducting bar. To prevent the strips dropping together by their own weight their free ends were burred over and thickened by pressure into projecting



FIG. 99.—Beeman's Support.

studs, which rested upon each other and maintained the spacing without interfering with the lengthways growth of the strips (see Fig. 99). The application of this method to perforated plates is shown in Fig. 100, a saw cut passing through the centre of each row of holes. Another alternative construction was to saw into the solid plate from both sides and leave the connecting bar in the middle instead of at one end.

According to an arrangement patented by G. E. Dorman in 1886, lead strips about $\frac{1}{32}$ in. thick were placed one upon the other with two or three small cross slips of some rigid insulating material between each to keep them apart, and the

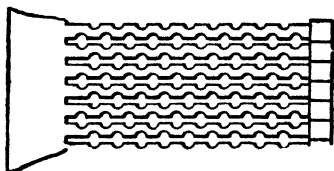


FIG. 100.—Beeman's Support.

space between these slips then further filled in with glass wool, horsehair, or other suitable substance, so as to completely insulate and separate the strips from one another. The strips were connected alternately to one of two main bars at either end, so that in reality an interlocked positive and negative electrode was obtained in the form of a flat plate.

Vertical Strip Electrodes.

The first of these was patented by De Kabath in 1881. Strips of lead, alternately flat and corrugated, were packed side by side and surrounded by a strip of stouter metal bent

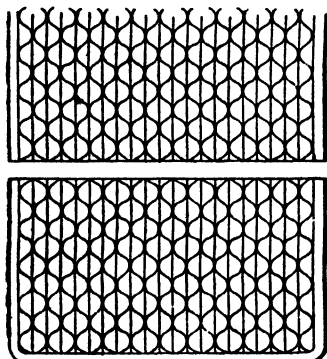


FIG. 101.—De Kabath's Strip Electrode.

into a rectangular frame, the whole being held together by transverse rubber bands. This electrode, a portion of which is shown in Fig. 101, appears to have been a very impractical

one both mechanically and electrically, for only the pressure between the strips and the frame was relied on to maintain the contact. It seems strange that a direct metallic connection was not established by burning or casting, as this would at once have put the electrode on a more satisfactory basis and anticipated some of the later constructions on the same lines.

De Kabath's other and better-known modification, in which the strips are enclosed in a perforated lead case, has already been referred to. Also in 1881 J. Carpentier and O. Pezzier

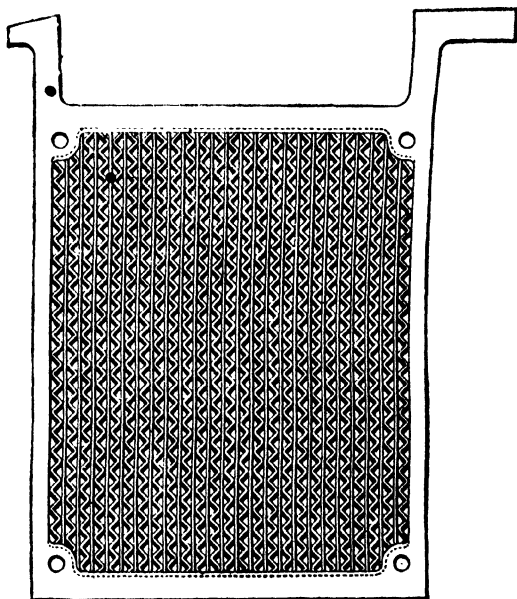


FIG. 102.—De Benardos' Electrode.

proposed an electrode which promised much better results than De Kabath's plate, but as it was claimed to be an infringement of his patent, it was never manufactured on a commercial scale. Narrow strips of lead were obliquely corrugated and folded double on themselves in long loops, so that the corrugations in adjacent layers crossed each other at an angle. A number of the loops were then packed side by side, and their free ends attached to a horizontal main bar leaving the loops hanging downwards.

These two devices for spacing strips by using them either alternately flat and corrugated, or obliquely corrugated in opposite directions, have been introduced over and over again in electrodes which differ very little from the earlier forms. Of the former type, N. De Benardos' plate, patented in 1887, is an example, but, unlike De Kabath's electrode, the strips have a solid lead frame cast all round them (*see* Fig. 102). P. J. R. Dujardin described a plate of the latter type in 1886. As an alternative to obliquely corrugating the strips they could be provided with projecting points at intervals to keep them apart, and in either case the whole of their surface was embossed with minute cells or indentations to afford a better

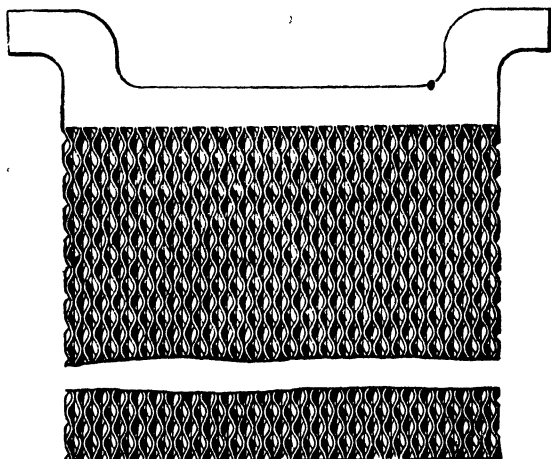


FIG. 103.—Paget's Electrode.

hold for the active material. The strips were united to horizontal bars both top and bottom, but these were not rigidly connected in any way, so that the plate could lengthen unimpeded. Fig. 103 shows an electrode proposed by L. Paget in 1888 which is almost identical in construction with Dujardin's.

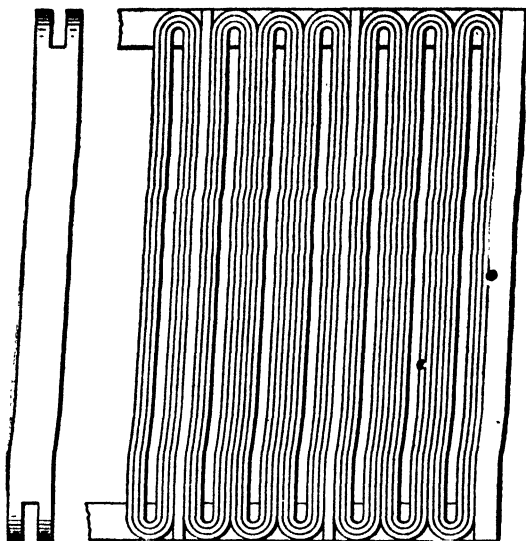
Coiled Strip Electrodes.

It is interesting to note that one of the first electrodes of this type was patented in 1882 by S. H. Emmens, whose name has since been somewhat brought into prominence by his claims for a method of converting silver into gold. He either coiled

strips into flat spirals which were mounted horizontally above each other with porous separating discs between, or else they were wound, edgeways on, as cylindrical spirals, and arranged concentrically round each other to form cells. In neither case does any special provision appear to have been made for keeping apart the surfaces of adjacent layers of tape. In the same year Beeman, Taylor, and King constructed electrodes by winding tape into flat spirals and then placing them in rectangular surrounding frames of stout lead. The whole of the turns were united together and to the frame by burning at the corners. At first the lead strip was prepared with rough, or uneven surfaces or of varying thickness by turning it out of the solid with suitable cutting tools. A second method adopted was to wind strips of insulating material, covered with layers of carbon or other inert substance, in between the lead tape, but, finally, in the cells used in connection with the B.T.K. system of lighting at Colchester in 1884, alternate layers of plain and corrugated strip were employed for the electrodes. The latter arrangement was also adopted in some cylindrical spiral electrodes patented by the same inventors. In 1884 Glaesener also proposed the use of electrodes of strip wound in flat spirals, but arranged horizontally, as in Emmens' plates, to which they were very similar. The surfaces of the strip were, however, embossed all over with small circular projections for spacing purposes:

In 1892 W. Morrison patented some forms of coiled strip electrodes constructed rather differently to those previously described. Several lead ribbons were placed together and wound into a narrow oblong spool on a core or shuttle, which was afterwards withdrawn, leaving an open space between the two sides of the coil. The spool was then notched top and bottom at right angles to the width of the ribbons, as shown in Fig. 104. A number of spools having been arranged side by side, main connecting bars were inserted into both sets of notches and sweated on to them, while these bars were further united at the ends by cross pieces so as to form a complete frame round the spools. Fig. 105 illustrates a portion of an electrode of this kind, but provided with additional cross ribs at intervals between the spools to further strengthen the plate.

An alternative construction to winding separate spools was to use several continuous lengths of ribbon and bend them back-wards and forwards zig-zag fashion, leaving open wedge shaped



FIGS. 104 and 105.—Morrison's Electrode.

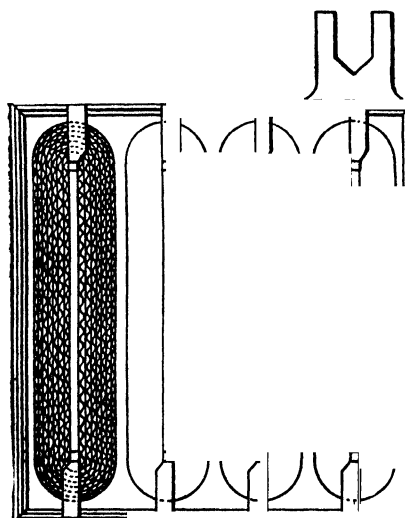


FIG. 106.—Blot's Electrode.

spaces between adjacent turns. This latter method was adopted by the American Battery Company, who at one time manufactured these electrodes, but they corrugated the ribbons before using them in order to provide proper spacing between the different layers.

A more recent coiled strip electrode was patented by G. R. Blot in 1894. Fig. 106 gives a side view of a plate constructed according to one of the methods described. In this case also the ribbons are wound into oblong spools, but the core pieces are of some hard lead alloy, and remain in the spools as part of the support, being provided with extensions top and bottom on to which the surrounding frame is cast. Two ribbons are wound together, the one corrugated and the other embossed

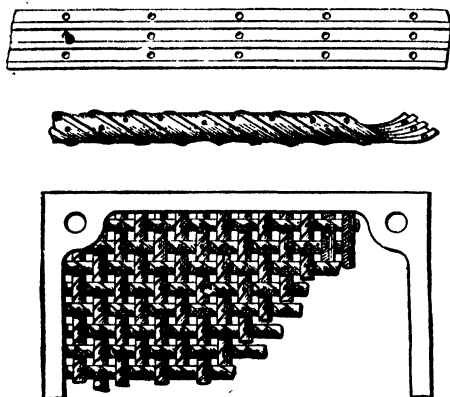


FIG. 107.—Colgate's Electrode.

and the whole of the turns are directly attached to the core piece by burning. In a modified arrangement, to which preference appears to be given on account of the better allowance for expansion, the layers of strip hang quite free instead of passing round the bottom end of the core piece.

A rather peculiar method of construction was patented by A. E. Colgate in 1892. Instead of weaving a gauze fabric from solid wires in the usual way, he employed hollow strands prepared from strips of perforated corrugated lead twisted up spirally, something after the manner of the paper spills used for pipe lights. The corrugations preferably ran in the longitudinal direction of the strips. Fig. 107 shows a portion of one of the

strands before and after twisting, and also a part of an electrode constructed from them. In this instance only one layer is employed, but for thicker plates two or three, one upon the other and slightly consolidated by pressure, could be used.

Arrangements of lead wire specially intended for Planté electrodes were proposed by Tommasi and also by E. Arnould and R. Tamine in 1883. Most other wire electrodes have been of the Faure type, and they are already described on page 71.

Porous Electrodes.

In the early days of lead storage cells many attempts were made to produce practical electrodes offering a large exposed surface for electrolytic formation by giving them a spongy or porous structure. A favourite method of obtaining this result was by alloying or mixing the lead with some metal or other substance which could afterwards be removed by suitable treatment. In 1881 Tommasi alloyed tin and lead for this purpose, and then dissolved out the tin with acid, while in the same year R. E. B. Crompton and FitzGerald patented the admixture of many other metals, including potassium and sodium, or of salts such as ammonia sulphate, magnesia, chalk, &c., the solvent used being varied as required. Zinc appears to have been a specially suitable metal in this connection, for it was again proposed by A. Watt in 1882 and D. Monnier in 1883.

A slight variation of the same principle was to cast the molten lead round some suitable salt loosely packed in a mould, T. Cuttriss employing soda in this way in 1882, and C. H. Thompson, common salt in 1888. The latter substance has again been utilised more recently by Pollak in 1896, but in this instance the salt is packed in the mould round a core piece, which represents the support or grid, and this being withdrawn before the lead is poured in, an electrode is obtained consisting of spongy portions divided up and held together by a solid frame.

Another modification suggested by FitzGerald, Biggs, and Beaumont in 1882 was to admix the lead with some metal, such as copper, in the form of filings or wire gauze, and then dissolve out as before.

An altogether different construction of porous electrodes, of which many varieties have also been proposed, consisted of

metallic lead in some finely divided form, but consolidated by pressure into a united mass of sufficient mechanical strength. FitzGerald, Biggs, and Beaumont obtained patents for electrodes prepared in this way from granulated or pulverised metal. A very favourite material for the purpose was lead in a state of dust. This could be obtained in several ways. In 1881 G. Grout and W. H. Jones described its production by violently agitating molten lead with charcoal or other powdered substance while cooling. Epstein employed the same method in the following year, but preferred to admix potassic permanganate, which gave off oxygen under the effects of the heat, and so more thoroughly aerated and subdivided the lead. Also, in 1882, Watt subdivided the molten metal by the action of a jet of steam or water, and by blowing it against a flat sheet he formed it into cakes or plates of any desired thickness. In the same year C. V. Boys used lead dust for electrodes, but coated it with mercury before making up into plates.

Fine wires or shavings of lead were also frequently employed for the construction of these consolidated plates; Pitkin, in 1881, being one of the first to use the latter form of the metal. In 1882 N. C. Cookson in England, and shortly afterwards Simmen in France, employed tangled masses of extremely fine wires so thoroughly intermingled as to form a kind of lead wool or felt. In both instances it was prepared in substantially the same way by applying pressure to molten lead and forcing it through extremely fine holes in the containing vessel. The wires were either cooled off in the air or received into water, and in the latter case, if it was desired to promote the oxidisation of their surface at the same time, suitable chemicals could be added. If, on the other hand, oxidisation was to be entirely prevented, nitrogen was substituted for air. This lead wool was made up into electrodes by enclosing a quantity of it in a perforated lead case; but in a modification of Simmen's plate, brought out in conjunction with Reynier, the perforated case was abandoned, and, instead, the lead wool was first subjected to a considerable pressure to mat it together and consolidate it, and then a stout frame of lead was cast round. Fig. 108 shows this electrode.

In 1882 R. H. Woodley and H. F. Joel prepared bundles of felted fibres of lead by cutting extremely fine shavings from

sheets of the metal. They were then attached to either side of a sheet of lead, and the whole consolidated by pressure. According to another method, patented by Joel in 1884, the bundles of fibres were interlaced or threaded through holes in a perforated back plate. The same idea was also embodied in plates described by P. Bailly in 1886. Another felted wire plate was patented by Heyl in 1889. It consisted of a number of independent porous masses held together by a solid frame which was cast round them. In many of these consolidated electrodes, oxides or other salts of lead, such as the sulphate, were mingled with the metal before subjecting it to pressure, in order to lessen the time occupied

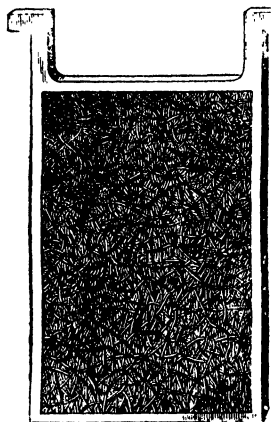


FIG. 108.—Simmen-Reynier Electrode.

in the first formation of the plates; but this practice must have been detrimental to the conditions necessary to obtain a successful result. On the one hand it would reduce the porosity of the electrode, while on the other hand it would prevent the various portions of lead from properly uniting to form a truly homogeneous mass, and thereby fatally affect its durability.

Another method of constructing porous plates, different to any of those already described, is that patented by F. T. Williams and J. C. Howell in 1883. Molten lead was cast into a perforated mould, and at the moment when the metal had partly solidified the portion still remaining fluid was

allowed to run off, leaving behind a highly porous mass of crystalline lead. For the convenience of manufacture, large blocks were prepared in this way, and then sawn up into plates of the desired thickness. Under this patent the well-known "Crompton-Howell" plates were manufactured, and so far they are almost the only variety of porous electrodes that has been used commercially on any extended scale.

In 1882 O. Schulz prepared electrodes with porous surfaces by covering lead plates with sulphur and heating them to bring about their more or less complete conversion into lead sulphide or sub-sulphide. They were then placed in dilute sulphuric acid and the sulphur abstracted electrolytically, chiefly in the form of hydrogen sulphide, leaving porous metal behind. This principle has since been utilised by A. J. Marquand, but in his process portions of the electrodes are protected from the action of the sulphur by covering them with enamel or other suitable means, thus providing for the maintenance of strengthening ribs of solid metal.

Arrangement of Electrodes.

Cells containing electrodes in the form of flat plates mounted vertically and parallel to each other, positive and negative alternately, and separated by upright rods or forks, were used by Planté in 1868, and this plan is now almost exclusively adapted, but it may be useful to call attention to a few other arrangements which have been introduced at various times and are of interest either historically or by reason of some special feature embodied in them. Planté's original form of cell, which he described in 1860, consisted of two long sheets of thin lead rolled up into a close spiral with a layer of flannel between them. This cell is shown in Fig. 109. After trying the parallel plates arrangement just mentioned, he returned in 1872 to the spiral form, but this time with horizontal rubber strip separation. Fig. 110 illustrates a pair of these electrodes about to be rolled up on a temporary mandril, and also when completed ready to go in the containing vessel. Some of Faure's earliest commercial cells were also made up with spiral electrodes, very closely following Planté's original method, and a battery of such cells was provided for the tests made in connection with the Paris

Electrical Exhibition of 1882. Fig. 111 shows a cell of this kind with the electrodes encased in some porous fabric.



FIG. 109.—Planté's Spiral Electrodes with Flannel Separation.

Although cells with spiral electrodes were very soon abandoned there have since been a good many proposals

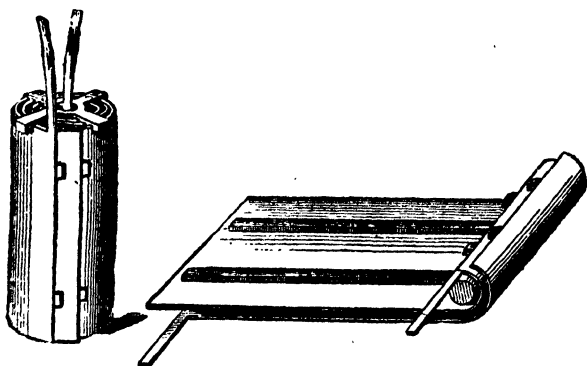


FIG. 110.—Planté's Spiral Electrodes with Strip Separation.

to use cylindrical electrodes mounted in pairs concentric to each other, but none of these need any detailed notice. The

same idea was adapted by Washburn in a somewhat modified form, and Fig. 112 shows a set of six pairs of his electrodes.

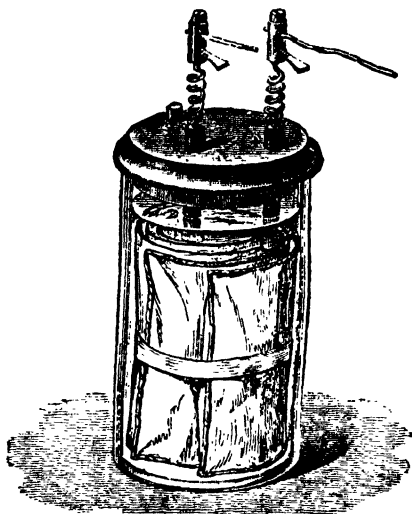


FIG. 111. —Faure's Spiral Electrodes.

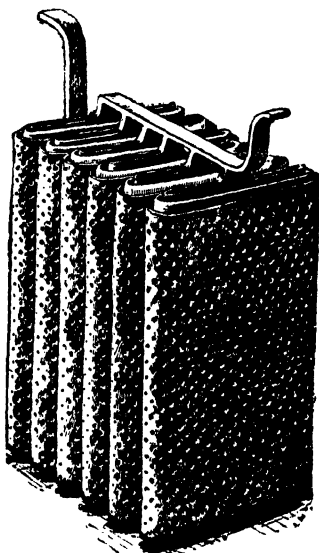


FIG. 112. —Washburn's Electrodes.

These consist of narrow oblong receptacles of perforated lead. The positives are each contained by a porous earthenware cell of a similar shape to themselves and filled with active material, the porous pot in its turn being surrounded by the negative with active material packed in between them. The outer electrodes all being of the same polarity there is, of course, no objection to their touching each other.

Rectangular or box-shaped electrodes arranged concentrically one within the other were used by Elieson in some of the earlier types of his "Lamina" cells.

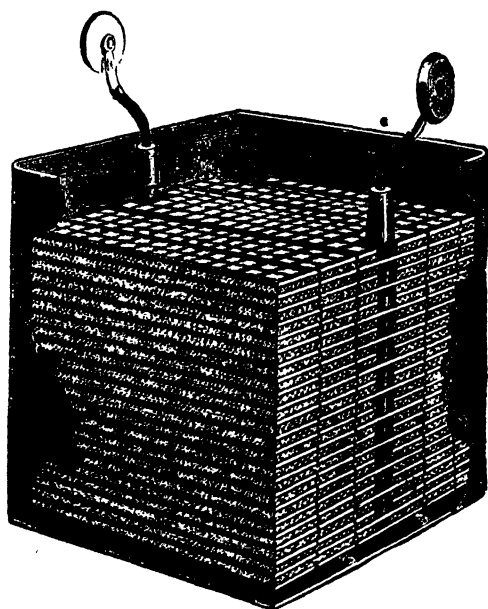


FIG. 113.—Pumpelly's Cell.

Numerous attempts have been made to employ electrodes in a horizontal instead of a vertical position. Khotinsky's strip electrodes, already described on page 36, were arranged horizontally in various ways in his early cells. Fig. 113 gives an illustration of a cell with horizontal electrodes which was brought out by J. K. Pumpelly in 1889. The plates were of the grid type and separated by sheets or mats of porous

cellulose or other material. In the same year horizontal arrangements were also proposed by Gibson and by V. H. Ernst. The former employed stamped sheet electrodes of the type already illustrated on page 67, Fig. 65, while the latter used electrodes containing cylinders of active material, which were hollow to allow the electrolyte to circulate internally. Also, in 1889, R. Eickemeier described a cell with horizontal electrodes, one form of which is shown in plan and vertical section in Fig. 114. Grids with hexagonal cells were filled with active material, but during the pasting process a round pin or core piece projected into each cell, so that when they were withdrawn a circular hole was left in

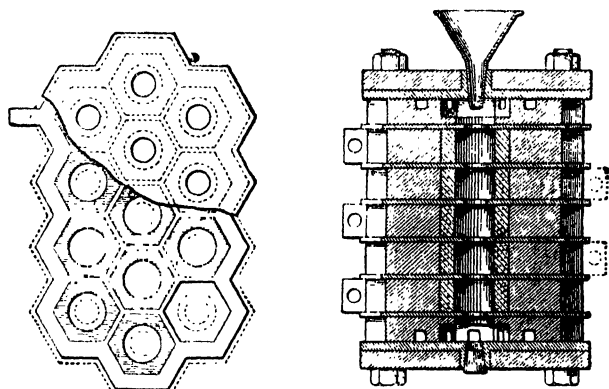


FIG. 114.—Eickemeier's Cell.

the centre of each pellet. The electrodes were then piled upon one another with these holes in vertical line, and having between each a diaphragm of insulating material also perforated with corresponding holes, but of slightly smaller diameter. End pieces or plates were provided at the top or bottom of a set of electrodes, and the whole clamped together by means of long bolts passing through them. In this way a series of self-contained vertical tubes or channels were formed to hold the electrolyte, which was inserted into the cell through an opening in the top plate communicating directly with the central channel, and distributing from that into the others by means of cross channels or grooves in the

bottom plate. Similar grooves in the top plate served for the escape of gas when charging. In the illustration a funnel is shown in position ready for filling the cell, and the plan gives a view of one of the electrodes partly covered with the separating diaphragm. In 1890, C. Hering patented a cell constructed on somewhat similar lines to the one just described. This was known as the "Atlas" cell, and is illustrated at Fig. 115. Here, also, the electrodes were mounted horizontally and only separated by thin diaphragms

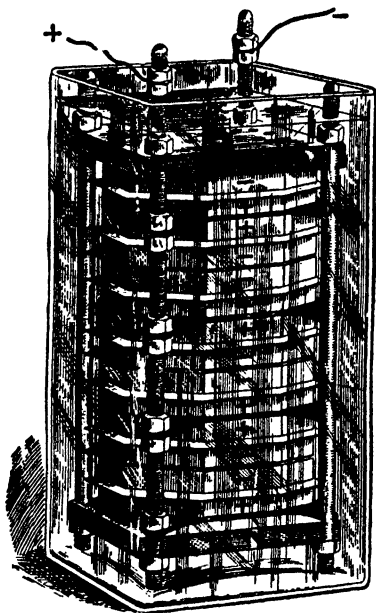


FIG. 115.—Hering's "Atlas" Cell.

of insulating material, and the working electrolyte was contained in vertical channels passing through the electrodes and separators. There were, however, a number of differences in detail. Each electrode consisted of a pair of discs or blocks of perforated active material placed on either side of a central sheet of thin lead similarly shaped and perforated. Nor was it attempted to make the channels liquid tight and self-contained, for they passed right through the top and

bottom clamping-plates, which were suitably perforated, and communicated with a further supply of electrolyte in an outer containing vessel. The clamping bolts were also used as main conductors, being of white metal, threaded from end to end, and carrying a number of nuts, between pairs of which the corners of the conducting sheets were firmly gripped. Fig. 116 shows another arrangement proposed by

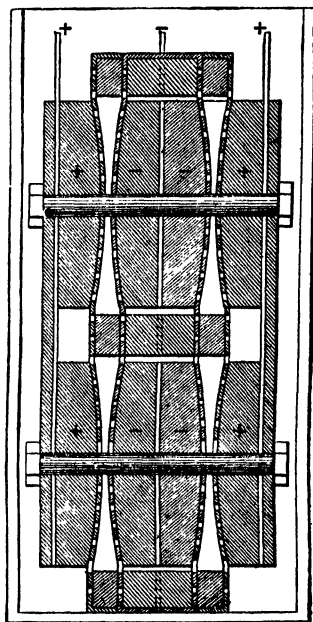


FIG. 116.—Hering's Cell.

Hering, in which independent blocks of active material were held against conducting plates by means of clamping bolts, but in this case the electrodes were mounted vertically.

A curious arrangement of electrodes was patented by Sellon in 1885 having, as he described it, the one set of electrodes transverse to the other set. Fig. 117 shows the construction he illustrated, which consisted of horizontal positives and vertical negatives. The positives were composed of a pile of sheets of corrugated lead having long slots

cut out of them to receive a set of ordinary grid negatives. In the drawing, the positives are shown filled with active material on one side only to allow for a better circulation of the electrolyte. The same idea has been utilized by Julien in 1896, but he proposed to employ rod-shaped negatives consisting of small cylinders of active material slid on to a central conducting stem. Each negative rod dropped into a

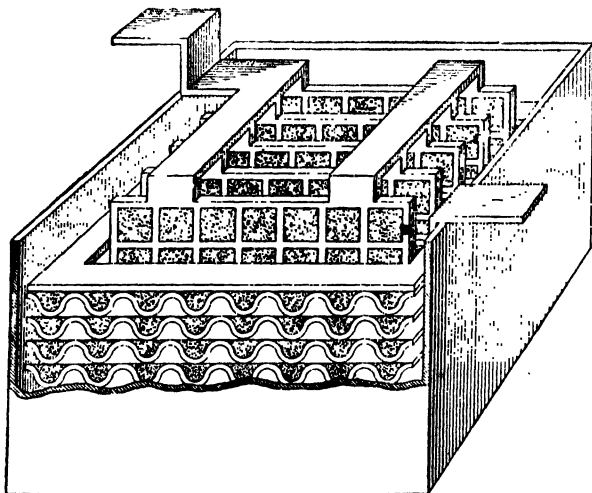


FIG. 117.—Sellon's Transverse Electrodes.

separate square tube or opening cut out of the horizontal corrugated sheet positives. In 1898 J. Burns also patented a very similar arrangement, but he reverted to plate negatives very closely on Sellon's lines.

Series Batteries.

"Series" or "high-tension" batteries derive their name from the rather peculiar arrangement of the cells composing them. Each electrode serves as a combined positive and negative for two adjacent cells—positive on one side and in one cell, negative on the other side and in the next cell—consequently, each cell can only comprise two electrodes, or more strictly speaking, two halves of two electrodes; and the total number of electrodes in the battery is the same as the number of cells plus one. By this means the electrodes

may be made to serve, either partially or wholly, as their own containing vessels, and all connections from cell to cell are dispensed with. There is a simplicity about such a device which has a considerable attraction for inventors, and very many attempts have been made to render it practical, but in spite of certain advantages which the arrangement undoubtedly affords, the mechanical and electrical difficulties in the way have hitherto prevented any form of battery of this type from securing a permanent position as a commercial article.

In 1881 Faure proposed several kinds of series batteries which are typical of most that have followed since. The simplest plan is described in his first English patent for pasted electrodes. A number of flat plates of lead having both sides covered with active material, except a clear margin round their edges, were set parallel to each other, with rubber washers of sufficient thickness in between them and fitting round three sides of the margin. The whole set of platts and washers were clamped up between two end boards by means of long bolts and nuts, and in this way a number of narrow cells were produced, of which the electrodes formed the sides and the rubber washers the ends and bottom. Any number of these cells could be made up in a set, according to the size most convenient and the voltage required, the current being drawn from the two end electrodes.

It is not necessary to refer to more than one or two of the series batteries that have since been proposed on these lines, as they only differ from each other in details of construction.

In 1891 N. Wladimiroff described a series battery on the same principle but with circular electrodes, having concentric grooves on both sides to contain the active material. The rubber separating washers were also circular, and formed completely closed cells between the electrodes except for a small hole through each washer, which served for the introduction of the electrolyte and the escape of gas. Amongst more recent series batteries are those patented by Schanschieff in 1894-5, and by R. Kennedy in 1896-7. It has generally been considered imperative that the supports should interpose a complete screen of metal, impervious to the electrolyte, between cell and cell; but in Kennedy's

earlier design he proposed in some cases to have his positive and negative active materials in direct contact and porous throughout. The same plan has since been suggested by others.

In 1898 N. H. Edgerton patented a series battery in which the flat sheet electrodes covered with active material on both sides are placed horizontally one upon the other, with layers of asbestos and charcoal between them. No outer vessel is provided, and no boundary washers, as the whole of the electrolyte is contained and held by the absorbent materials.

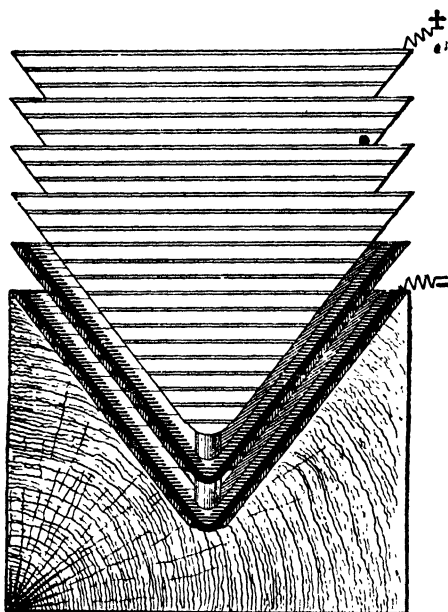


FIG. 118.—Phillippart's Series Battery.

There have been a few series batteries proposed in which the partitions between the cells are of ebonite, celluloid, or other suitable material with metallic supports permanently connected together on either side of them. Faure described something of this sort in one of his early patents. The partitions were of wood recessed on each side to take a lead plate let in flush with the surface and with connecting straps

of lead passing over the top. P. Ribbe patented a series battery in 1895 in which ebonite partitions built up in two parts had lead studs embedded in them, and on to the ends of these studs where they projected through the partition, pieces of lead with radiating arms to distribute the current to the active material were burned. H. Dolter, in 1898, also

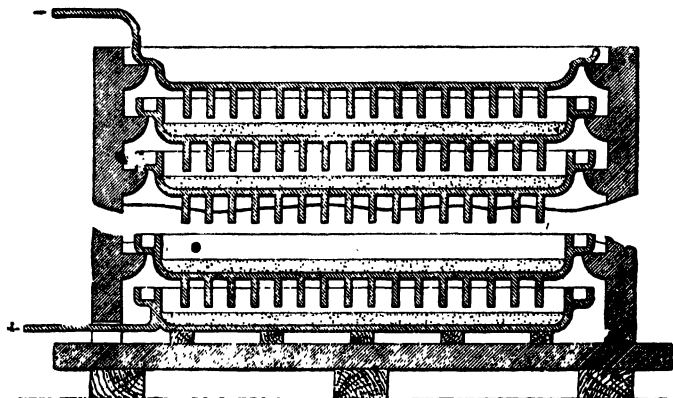


FIG. 119.—Sellon's Tray Form of Series Battery.

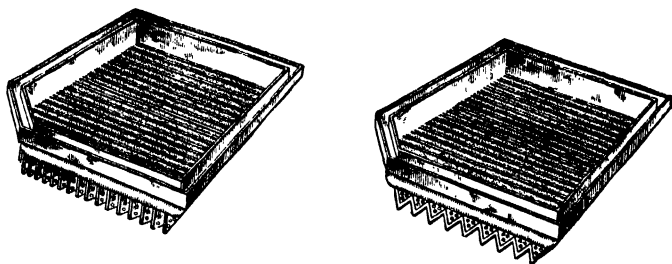


FIG. 120.—Trays for Sellon's Series Battery.

patented a series battery with ebonite partitions. Numerous lead studs passed through them and carried a series of lead washers on either end.

In another kind of series battery, which Faure patented in 1881, a number of conical cups of plain lead were placed one within the other, point downwards, and held apart by

suitable separators. In this arrangement the electrode constitutes the entire containing vessel. Fig. 118 shows a similar construction proposed by G. Philippart in 1883. The conical cups are provided both inside and out with horizontal grooves to hold the active material, and are kept from touching one another by insulating strips placed between them. Sellon also described a variety of designs for conical series cells in 1883-4, and a form of this type of electrode proposed by Julien in 1887 had horizontal ribs on the outside and vertical ribs on the inside. According to a modification patented by Sellon in 1886, the conical cups were replaced by shallow rectangular lead trays. Fig. 119 gives a vertical cross section through a set of these cells and Fig. 120 a perspective view of two designs of trays. Perforated ribs packed with active material project from the bottom of the trays and dip into the electrolyte of the cell underneath and the inside of the bottom is also provided with ribs. The trays have projecting rims by means of which they are supported independently of each other, and the top of the rim forms a gutter to collect acid drippings from the tray above it. One corner of each tray is flattened as shown, so that when necessary, electrolyte may be added to the tray below without any difficulty. The flattened corners come alternately right and left. Series batteries with trough electrodes were also patented by A. Tribelhorn in 1897.

CHAPTER III.

STORAGE CELLS OTHER THAN LEAD.

Although the lead/lead peroxide cell has so far proved the only accumulator capable of achieving any degree of commercial success, there have been numerous attempts to put into practical shape other combinations which, either by reason of their higher E.M.F. or their increased ampere-hour output, would afford a larger storage capacity in proportion to their weight. The whole of the attempts, however, have had to be concentrated upon a very few combinations, so limited are the number which, in any degree, fulfil the necessary conditions; and of these only the zinc/lead peroxide acid cell and the zinc/copper oxide alkaline cell have inspired sufficient confidence from their laboratory tests to obtain trials on a larger and more practical scale. Even then, as is well known, they have hitherto always had to be abandoned in the end by reason of their instability and rapid deterioration.

The Thomson-Houston Cell.

One of the first combinations specifically intended to be used as an accumulator, was patented by Elihu Thomson and E. J. Houston in 1879, and was an endeavour to produce a reversible Daniell cell. Two plates of copper were arranged horizontally, one above the other, in a saturated solution of zinc sulphate. The plates were some distance apart and a porous diaphragm was provided between them. On passing a current through the cell from the lower to the upper electrode, the former partially dissolved up and the electrolyte surrounding it became charged

with copper sulphate while, at the same time, metallic zinc was deposited on the upper plate. When this action had been continued long enough the cell was ready for use as a zinc/zinc-sulphate/copper-sulphate/copper combination, and a discharge could be taken from it proportionate to the first charge it had received, zinc being dissolved up and copper re-deposited. The diaphragm served a double purpose: partly to collect any loosely-deposited zinc that might become detached, but also to retard as much as possible the diffusion of copper sulphate into the top layers of the electrolyte. Obviously such a cell would depreciate very rapidly, for, in addition to the difficulty of maintaining an effective re-deposition of both metals for more than a few times, it would be impossible to prevent copper sulphate from soon reaching the zinc electrode and giving rise to excessive local action there from precipitated copper. It must be remembered, however, that this cell preceded Faure's improvements in lead accumulators and had only the rather unpractical Planté cells of that period to compete with.

Sutton's Cell.

Faure's discovery naturally gave a great impetus to the search for other and better reversible cells, and in 1881, while the excitement over the possibilities opened up by the new means of storing electricity was at its height, the first of these was announced from Australia. This was the proposal of H. Sutton to use electrodes of copper and of amalgamated lead, the former of which constituted the cell box itself and contained a solution of copper sulphate. The lead electrode was the positive and became superficially peroxidised on charging, as in a Planté cell, copper being deposited at the negative; so the combination resolved itself when fully formed into one of copper/sulphuric acid/lead peroxide—that is, the ordinary accumulator with its spongy lead plate was replaced by copper. The lead was amalgamated in order to facilitate its peroxidisation, for it was claimed that, in this condition and in the copper sulphate electrolyte, its formation proceeded with great rapidity and without the need for any reversals. Indeed, apart from the merits of Sutton's combination as a

whole, it was suggested that his procedure could, with advantage, be used to form the plates for ordinary Planté cells; but presumably it did not realise anticipation, for it appears to have been quite forgotten.

Reynier's Copper/Lead Peroxide Cells.

In 1882-3, E. Reynier attempted to put the Sutton combination into more practical shape. In his first form of cell the positive consisted of one of his pleated sheet electrodes, illustrated on page 90, and was suspended between two

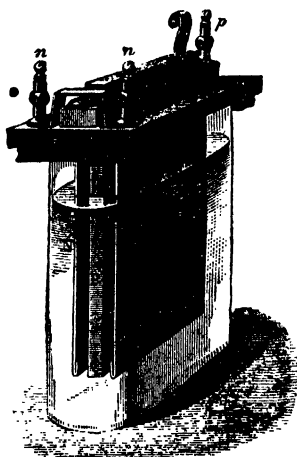


FIG. 121.—Reynier's Copper/Lead Peroxide Cell.

plates of unamalgamated lead upon which copper was deposited on charging. This design is shown in Fig. 121. He afterwards constructed cells in which large shallow lead trays formed the containing vessels, and also served as the negative electrodes. Each cell contained one large positive of the pleated sheet type, placed horizontally. The advantage claimed for this arrangement was that any loose copper always remained in contact with its electrode and could be dissolved up on discharge instead of, as in the previous type of cell, falling to the bottom of the vessel and not entering into solution again.

Since Reynier's experiments, nothing further seems to have been done with this combination. Its E.M.F. is only about 1.25 volts, so that the increase in the ampere-hour output, obtained by substituting copper for lead as a negative, is considerably reduced when the total or watt-hour output for weight is considered; and it has been found that the small resultant gain in this respect is more than counter-balanced by the troubles invariably associated with a soluble electrode and the regulation of its metallic deposit. There is, of course, no fear of the copper sulphate giving rise to local action, as in the Thomson-Houston cell, for in this case the copper is the negative instead of the positive electrode.

Zinc/Sulphuric Acid/Lead Peroxide Cells.

This combination might be derived from the previous one, or from the ordinary lead accumulator by the obvious expedient of substituting as the negative active material some metal which afforded an higher instead of a lower E.M.F. than lead; and for this purpose zinc has always proved more suitable than any other. As a matter of fact, the unusually high E.M.F. of this couple attracted attention long before storage cells were much thought of, and several investigators utilised it for primary cells in which chemically-prepared lead peroxide formed the depolarising agent. In 1879 and the two following years, A. d'Arsonval and J. Carpentier proposed various rudimentary forms of reversible cells with negatives of zinc deposited on carbon or mercury electrodes. In 1882 K. E. Boettcher described a cell containing electrodes of unamalgamated thin sheet zinc and of lead foil pasted with lead oxide in an electrolyte of zinc sulphate, and in the same year C. H. Cathcart patented a cell with lead positives and corrugated perforated sheet zinc negatives, both electrodes being amalgamated. The important part played by mercury in improving the quality of the zinc deposit and preventing its destruction by local action appears to have very soon been recognised. In this patent of Cathcart's, the procedure to be followed is given in considerable detail. First he amalgamated the sheet zinc, then deposited electrolytic zinc upon it, and then again amalgamated. The electrode was now ready

for more zinc to be deposited upon it in the ordinary course of charging, the idea being never to dissolve up the layer of pure zinc first put on. In 1883, O. Lodge described the use of amalgamated alloys of zinc and mercury as electrodes, and also the deposition of similar alloys from solutions of their mixed sulphates, both on to zinc supports and also upon the spongy lead of ordinary lead negatives. Very similar devices for negatives were used by P. Bailly in conjunction with his lead wool positives already referred to on page 102. Both Reynier and Tamine proposed to add ammonium sulphate to the electrolyte in addition to mercury sulphate, in order to diminish the wasting of the zinc by local action, and later on P. Benjamin, with the same object, deposited the zinc on lead plates which had first been gilded.

Reynier's Zinc/Lead Peroxide Cells.

But again it was Reynier who in 1883 first put the combination into anything like practical form. His cells only contained two electrodes. The positive was of his pleated sheet type but bent round so as to form a hollow cylinder. This was placed in a circular wicker-work cage

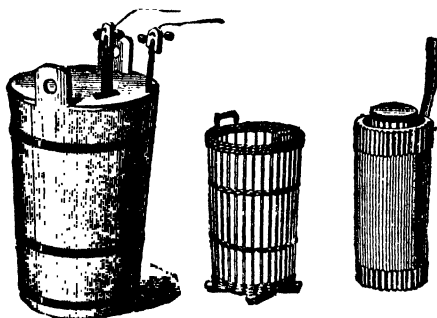


FIG. 122.—Reynier's Zinc/Lead Peroxide Cell.

which served as separator, and went inside a cylindrical negative of sheet lead, the whole being contained in a round pine-wood pail, tarred on the inside. It is evident from this description that the arrangement was somewhat primitive, but as a matter of historical interest it is illustrated in Fig. 122. On the right is the cylindrical positive, strengthened

top and bottom by folding over the sheet lead before pleating to provide an extra thickness of metal there. In the centre is the wicker separator standing on a wooden cross-piece, and on the left the complete cell in its outer vessel bound with copper straps.

In his next design Reynier adopted the more usual arrangement of flat electrodes parallel to each other, and for that purpose he employed pleated positives of the kind shown in Fig. 95, page 90, and negatives of amalgamated sheet lead. To maintain an efficient amalgamation, the sheet was folded so as to provide receptacles or pockets in which pieces of solid zinc-mercury amalgam were placed. Still later, the pleated positives illustrated on page 91, Fig. 97, were adapted in combination with a negative constructed from one continuous piece of sheet lead folded zig-zag fashion and passing in and out between the positives. The pockets containing amalgam were abandoned, and instead a solution of mercury salt was added to the electrolyte.

Main's Cells.

From about 1887 up to 1892 a most determined and sustained attempt was made in the United States by W. Main to produce a practical form of cell with zinc negatives. During the earlier part of the time he worked with A. V. Meserole, and their cells were used by the River and Rail Electric Light Co., of New York, to run electric tramways. Throughout, the positives consisted of one form or another of Main's electrode, built up from layers of perforated lead foil riveted together as described on page 89. At first, the surfaces of the foil were covered with powdered graphite, but afterwards some substance, such as zinc sulphate, which would dissolve out and leave space for expansion between each layer, was adopted. A number of different designs of negative electrodes were successively experimented upon. To begin with, vertical sheets of plain zinc were used in an electrolyte of zinc and mercury sulphates. Then the zinc sheets were riveted to sheets of amalgamated copper; and in 1889 Main patented some modified constructions, in which the electrodes

were arranged horizontally, partly to maintain a better amalgamation and partly to minimise the effects due to inequalities in the density of the electrolyte. One design of cell is shown in horizontal and vertical cross-section in Figs. 123 and 124. The negatives consisted of shallow perforated trays of amalgamated copper, and contained a sponge or amalgam of zinc and mercury. The electrodes rest on horizontal rods of ebonite, which are themselves held

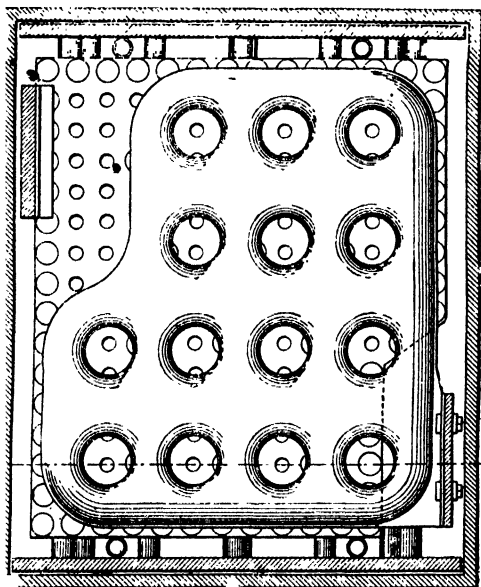


FIG. 123.—Main's Cell. Horizontal Section.

by two vertical side-plates of the same material. It will be noticed that the perforations in the copper trays are of comparatively large size, and have their edges turned up to the same height as the rim to prevent the amalgam from falling through them. Neither the positives nor the negatives are quite rectangular, but each has a corner missing to avoid the possibility of short-circuiting where the main connecting bar of opposite polarity would otherwise come very close.

In a later type of cell, patented in 1892, Main returned to vertical electrodes. Fig. 125 gives a view of this

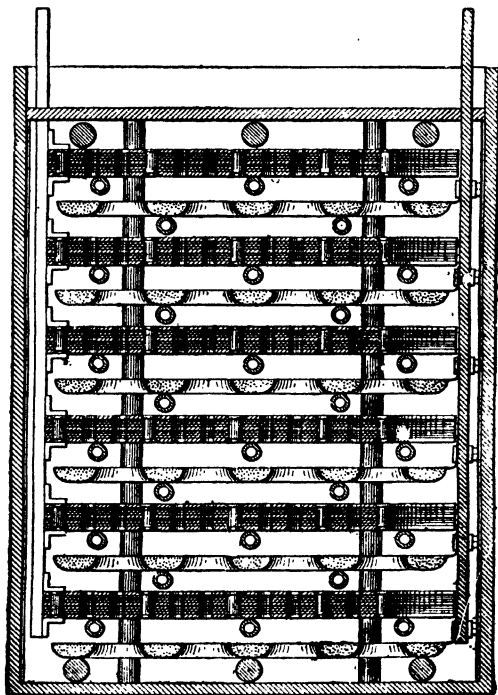


FIG. 124.—Main's Cell. Vertical Section.

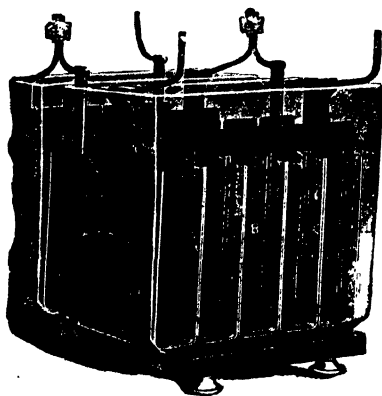


FIG. 125.—Main's Cell with Vertical Electrodes.

arrangement. The negatives, still of amalgamated sheet copper with large perforations, had the sponge of zinc and mercury deposited upon them electrolytically. Each positive was surrounded by a U-shaped negative, which passed underneath it; and each negative was riveted to the next to unite them all into one continuous piece. Sometimes plates of zinc were placed between the riveted copper sheets in order to provide a supply to start the cell, instead of adding zinc sulphate to the electrolyte. The bends of the negatives all rested on the bottom of the containing box, and some mercury was placed there to keep up their amalgamation.

Epstein's Zinc Cells.

In 1894 L. Epstein turned his attention to cells with zinc negatives, and especially to providing means for keeping the electrolyte in circulation in order to obtain a more uniform deposit of zinc. According to one patent of that year, he employed discs of amalgamated copper-wire gauze attached at their centre to a horizontal spindle, which was rotated either intermittently or continuously. This spindle also served as the main conductor to the negatives, and holes were left in the positives for it to pass through, suitable insulating pieces being provided at those points to prevent short-circuits. In a later patent of the same year the idea of rotating the electrodes themselves was abandoned, and instead paddles were attached to the spindle and rotated in between the positives and negatives, or rather the negative, for this was now arranged on Reynier's plan of a single zig-zag piece. In the following year Epstein proposed to place his agitator horizontally in a clear space left for that purpose at the bottom of the cell, and to actuate it by a vertical spindle. The copper gauze negatives stood in ebonite troughs containing mercury, while the positives were placed within perforated ebonite cases lined with asbestos fabric, in order to minimise as much as possible the liability to short-circuiting from detached particles of zinc.

Since 1895 several patents relating to cells with zinc negatives have been taken out by H. Leitner. These chiefly deal

with the addition of various sulphates to the electrolyte to improve the zinc deposit, and the general arrangement and construction of the electrodes. Within the same period a variety of devices for effecting and maintaining an efficient amalgamation have also been described, amongst others, by J. Julien and P. J. R. Dujardin.

The use of cadmium either in combination with or instead of zinc as the negative active material has been proposed at various times. In 1887 A. E. Peyrusson prescribed an acid solution of cadmium sulphate for the electrolyte, as also one of tin sulphate. In 1897 E. E. Lee patented a cell with cylindrical electrodes in which cadmium was deposited on a copper gauze negative from a neutral solution of cadmium sulphate, and since then a similar electrolyte has been employed by MM. Commelin and Viau.

Output of Zinc/Lead Peroxide Cells.

So far as the ratio of weight to output is concerned, the improvement that may be effected by the substitution of zinc for lead as the negative active material of a storage cell is very considerable, and is the outcome of several different causes. In the first place, a zinc/lead peroxide cell commences to discharge at 2.5 volts to 2.4 volts and finishes its useful discharge at about 2.2 volts, which means an increase of more than 20 per cent. in the average potential difference throughout. Then the combining weight of zinc (65) is less than one-third that of lead (207), and further, at least twice as much of the latter has to be provided as can be fully sulphated, while zinc, owing to the solubility of its sulphate, can furnish its full equivalent of energy, so that it is able to replace about six times its weight of spongy lead. Finally, as the zinc may be deposited on a support of amalgamated copper—a material far superior to lead both in respect of its electrical conductivity and mechanical strength—full advantage can be taken of the small quantity of active material that has to be carried, and the weight of the support itself reduced in an equal if not larger proportion. The total result is that zinc on copper negatives weigh but a small fraction of spongy lead on lead negatives of equal capacity, and by their use it

should be possible to double the watt-hour output per pound of some types of lead accumulators or, in any case, to reduce their weight by about one-third.

Defects of Zinc/Lead Peroxide Cells.

The defects which have prevented a combination that offers such great advantages from coming into practical use are, as might be imagined, of a very fundamental nature, and not ones depending merely on details of construction. They are chiefly due to the characteristic behaviour of zinc, and the extreme readiness with which it undergoes oxidation by local action. Impure or commercially pure zinc is rapidly attacked and dissolved by dilute sulphuric acid with a copious evolution of hydrogen. Chemically pure zinc is nearly, though not quite, insoluble in perfectly pure dilute acid, but the presence of the merest trace of many other substances, especially of oxidising agents or of salts of any metal electro-negative to zinc, enormously increases the rate of its solution.

The zinc employed in storage cells is almost invariably deposited from a solution of pure zinc sulphate in their own acid electrolyte, for it is more easily and cheaply obtained in a state of purity by this means than by any other. Assuming, however, the necessary purity of all the materials used, there still remain two special causes which greatly add to the difficulty of protecting zinc in an accumulator from local action. For one thing, there is certain to be some difference of potential between the deposited zinc and its support. Zinc cannot be deposited direct on to any of the usual metals without its being very freely attacked on open circuit; but if they are first amalgamated the action is reduced to a minimum, for the E.M.F. between zinc and zinc amalgam is very slight. It might naturally seem that metallic zinc would be the most appropriate material to receive the deposit, and it has been used for this purpose, but, apart from the cost when sufficiently pure, it is itself much too liable to be attacked and destroyed. Lead has the great advantage of not passing into solution under any conditions whatever, but, owing to its mechanical weakness, especially when amalgamated,

its weight cannot be sufficiently reduced to enable the benefit due to the use of zinc to be properly realised. Well-amalgamated copper has generally proved the best support for practical purposes. It may be made very light, takes a good deposit of zinc, gives rise to very little local action, and is not itself attacked under normal conditions. It is true the effect is most disastrous and the cell practically ruined if once it does get into solution, but if the causes that lead to this cannot be avoided the cell is no good anyway.

The second cause tending to aggravate the local action is the fact that no matter how pure the electrolyte may be at first, the very act of charging leads to the formation of persulphuric acid and other highly oxidised compounds which attack the zinc very readily. Nothing very definite is known as to the conditions most suitable or otherwise to the production of these substances, but it is quite probable that the presence of considerable quantities of zinc sulphate in the electrolyte may favour their generation and render them more stable when once they are formed. However this may be, it is certain that the local action is at its maximum in a freshly and fully charged cell, and, if every care has been taken to ensure the purity of all the materials, will gradually decrease on standing, even though there is still plenty of zinc left at the negative.

The loss of efficiency owing to the zinc dissolving up on open circuit is the least of the troubles brought about by local action, for if this were all it would still be well worth while to employ zinc negatives in cells for traction purposes where they can be discharged within a short time of their re-charging, and where a reduction of weight is the prime consideration. What is far more vital, it spoils and breaks up the zinc both while depositing and afterwards. During the earlier stages of the charge, when there is most zinc in solution and least free acid and secondary peroxidised products, and when the deposited zinc is nearest to the mercury on the support, it will probably form hard and adherent, and there will be little or no evolution of gas. But as the charge proceeds all these conditions are gradually reversed, the tendency for the zinc to re-dissolve becomes stronger and stronger and, it begins to deposit loose and powdery, or scaly, or soft and too spongy :

in any state in fact but the right one, and accompanied by vigorous gassing. After the re-charge is finished, the mischief still continues, or rather is completed. The combined action of the zinc dissolving up, and the gas bubbles continually coming off, undermines the deposit and detaches numerous metallic particles, of which the lightest and most spongy may for a time form a sort of scum on the surface of the electrolyte, but eventually they all collect in the bottom of the cell.

These deleterious effects are generally culminative, especially if the re-charges follow each other with but short intervals between ; and the deposit rapidly becomes worse in quality and less in quantity, for the loose metal accumulates faster than it can be re-dissolved in the heavy strata of zinc sulphate by which it is surrounded. Not only is the zinc floating about in the electrolyte very liable to give rise to short circuits as it settles down, but the same result is often brought about by the deposit forming zinc trees, which soon reach from one electrode to the other ; or, if the deposit is very soft and spongy, it will frequently creep towards the positives along any available surface, such as that of the separators, between them. Although this short-circuiting can be obviated to a large extent by a proper design and arrangement of the separating and protective devices, it may prove extremely troublesome in practice. When the short-circuits do occur, they may, if not attended to in time, clear all the zinc from the adjacent portions of the negative, and bring the copper of the support into solution. This is fatal, for the copper re-deposits in a spongy form and sets up a very powerful local action.

The same result may be brought about merely by leaving the cells in circuit after their discharge at normal voltage is completed. If the fall of potential is due to all the zinc having been used up at the negatives before the positives are exhausted, copper will begin to dissolve at once, the cells now behaving like copper/sulphuric acid/lead peroxide couples, and discharging at a little over 1 volt each. If, on the other hand, it is the positives that are run down, the cells will still continue to discharge, as, owing to the high E.M.F. due to the oxidation of zinc, they can maintain a current at something under half a volt

apiece until the positives are entirely reversed and converted into spongy lead electrodes. To do this, however, a very considerable excess of zinc is required, and should the supply give out while any unreduced peroxide yet remains at the positives, there will still be just sufficient E.M.F. to cause the copper to pass into solution. It would appear, therefore, to be most important to always maintain a plentiful supply of zinc at the negatives, but, for the reasons just now given, this is not easy to accomplish, especially as the thicker the deposit the greater the difficulty of keeping it in condition.

In spite of all its drawbacks, the zinc/lead peroxide combination remains at the present time the only alternative to the ordinary lead cell in any degree practicable. Its undeniable advantages are a great attraction, and may yet lead to some satisfactory solution of the problem it presents.

The Lalande-Chaperon Cell.

The inception of the zinc/potassic hydrate/copper oxide accumulator dates from the year 1881, when F. de Lalande and G. Chaperon patented the combination as a primary cell. They recognised the possibility of its reversal, however, for they say in their original patent, "The piles are reversible, that is to say, capable of being re-charged by an electric current of sufficient electromotive force," but apparently they were not acquainted with the modifications and precautions necessary to render the cell at all practicable under these conditions, and when their specification was amended later on this passage was struck out. The arrangement described by them consisted of a positive of iron, copper or other metal or of gas-retort carbon surrounded with copper oxide, which could be agglomerated by one of several described processes, with a negative of zinc, preferably amalgamated, and an electrolyte of 10 to 50 per cent. solution of caustic potash or soda.

According to a later patent of 1884, the construction is specified in more detail, and several modifications introduced. Cast-iron is given the preference as the material for the positive electrode, which also serves as the outer vessel,

and contains a layer of copper oxide in the bottom of it. Methods for rendering the cells air-tight to prevent action with the alkali while at the same time providing for the escape of gases are given. As before, zinc constitutes the negative electrode, but is wholly immersed in the electrolyte by means of a supporting rod of amalgamated brass. For use in cells to be re-charged, a special form of negative is proposed, consisting of a zinc or brass tray containing mercury with which the deposited zinc forms an amalgam.

Desmazuress' Cells.

In 1884 E. Commelin, G. Bailhache, A. de Virloy, and L. de Bousignac took out a patent for substantially the same combination as that of Lalande and Chaperon, but entirely confining themselves to its use as a storage cell. The copper oxide was mixed with plumbago or other form of powdered carbon, and applied to the surface of a carbon plate, which was then wrapped in a "hempen cloth" and placed between two negative electrodes of perforated sheet copper or copper gauze. In 1886 the same inventors, in conjunction with C. Desmazuress, obtained another patent for various modifications in the construction of their cell. The positive electrode now consisted of porous metallic copper, prepared either by eliminating the mercury from a copper amalgam by heat, or by subjecting electro-chemically precipitated copper to pressure and so consolidating it into a coherent mass, or by treating copper oxide in a similar manner and then reducing it with hydrogen or carbon monoxide. The latter result could also be attained by mixing and compressing the oxide with various organic carbonaceous materials, and afterwards subjecting the mass to heat. To give sufficient strength to the plates without making them too thick, a piece of copper wire gauze was inserted in their centre. The metals copper, brass, zinc and tinned or galvanized iron were all named as suitable for the construction of the negative electrode, brass being preferred. It could be used in the form of plain or perforated sheets, or wire gauze, and either amalgamated or unamalgamated. The electrodes were arranged horizontally, each positive being wrapped in parchment paper or canvas,

and they were kept apart by glass separator strips. The use of a galvanized or tinned iron containing vessel which could serve as part of the negative electrode, and the addition of alkaline chlorates to the electrolyte to improve the zinc deposit were also mentioned.

In 1887 a third patent was filed, this time by Desmazuères alone. It added little of novelty to the previous specification, but went into more details and specially emphasised the great pressure—4 tons to 8 tons per square inch—required to consolidate the copper dust into thin plates, apparently of solid metal, but in reality only of one-half to two-thirds its density, and therefore possessed of a considerable porosity. The negatives were of tinned iron wire gauze held in a tinned iron frame, and the electrodes were now arranged vertically, but, as before, separated by glass rods and parchment envelopes. This was the type of cell used in 1887-8 to supply the motive power for some experiments by the French Government with a submarine boat—*The Gymnote*—which excited much interest at the time.

The Waddell-Entz Cell.

As was the case with the zinc/lead peroxide cell, so also the zinc/copper oxide cell obtained its most practical trial in the United States, where it was known as the "Waddell-Entz" battery. Not only was it used in New York in 1893-4 for the entire working of a tramway line for some considerable period, but it was also introduced into Europe and employed for the same purpose at Hagen, in Germany, and at Vienna.

From 1889 to 1891 several patents were taken out by J. B. Entz and W. A. Phillips for a new type of copper oxide positive electrode. It was made up from a composite wire consisting of a copper wire core, then a layer of copper oxide, then a network of finer copper wires, in the meshes of which the copper oxide was embedded, and finally an insulating sheathing of braided cotton or other suitable material. The copper oxide was agglomerated by mixing it with sulphur, heating and then compressing it into the desired shape and position. Next a stronger heat was applied, which drove off the sulphur and left a mass of porous copper behind, and by

still continuing the heat in the presence of a free supply of air the copper could be once more oxidised. The composite wire was converted into electrodes by bending it to and fro on itself to form flat mats of the desired size and shape. Fig. 126 shows one such arrangement and the details of mounting it. The bottom and sides of the mat were surrounded by a U-shaped wire in the same plane as itself and attached to it at the points of contact by ties of twine. Then two other U-shaped wires at right angles to the first

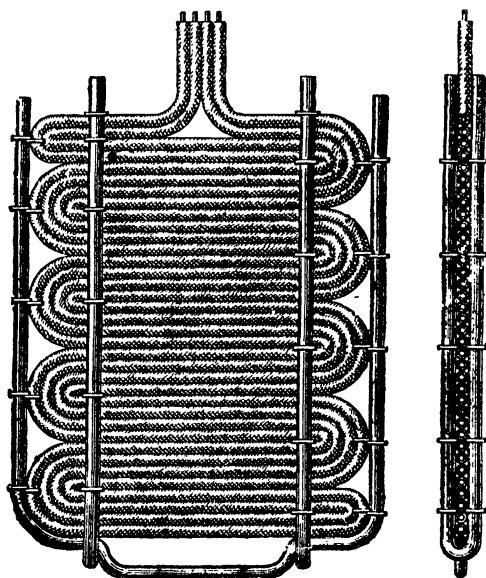


FIG. 126.—Waddell-Entz Positive Electrode.

were slipped over the mat, and the two limbs of each wire bound together by ties passing through it. In this way the whole electrode was held together and its parts prevented from shifting. The kink in the bottom of the first wire served as a support for the plate and to keep it at a proper distance from the floor of the cell, while the other two wires formed the separating strips. These mounting wires were composed of some textile material impregnated with a mixture of whiting and sodium silicate, and then treated in an

alkaline solution which set them to a stiff vitreous substance resembling stone.

This electrode was an endeavour to improve upon the type used by Desmazuers in two important particulars where the latter had proved to be defective. The one was to provide a solid conducting support throughout the active material, so that the electro-chemical action should be uniformly distributed over it even when the plate was at its stage of highest resistance—that is to say, when most fully oxidised—the other was to obtain an active material of greater porosity in order to minimise as much as possible the injurious chemical actions so liable to be set up in its pores.*

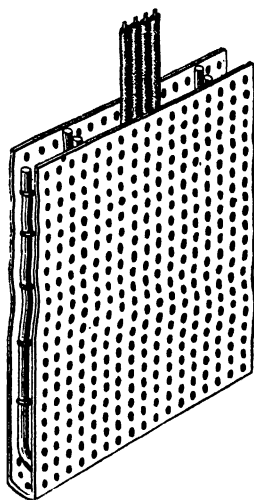


FIG. 127.—Waddell-Entz Negative Electrode.

The negative electrode or support for the deposited zinc consisted of a perforated sheet of tinned iron bent double on itself, and in the space thus formed between its two sides, the positive electrode was placed, as shown in Fig. 127. The negatives rested directly on the bottom of the containing box, which was also made of tinned iron, and constituted one terminal of the cell.

In 1892 another patent was obtained for heating the alkaline electrolyte during the discharge and re-charge of the cells

in order to promote its circulation and render the action on the electrodes more uniform, but it also served the equally important purpose of preventing the formation of injurious peroxidised compounds. It was found necessary to adopt this procedure in the cells used on the tramways, a temperature of about 130°F. or 55°C. being maintained. In 1893 Paul Schoop, who had devoted a good deal of attention to the Waddell-Entz battery and the construction of cells embodying the same combination, described and patented various arrangements in which the electrolyte was circulated by mechanical means.

Alkaline Cells with other Negatives.

Although copper is the only metal whose oxide has been employed on any practical scale as the positive active material or depolarising agent in an alkaline electrolyte, many others have been proposed and tried. Indeed, in some of the early patent specifications relating to cells of this kind, most of the ordinary metals are enumerated, quite regardless of the known unsuitability of many of them, and with the idea no doubt of covering the use of everything that might prove in the least degree possible at any future time. A few oxides, however, have received more specific attention. In 1886 H. Aron took out a German patent for an alkaline cell with zinc and oxide of mercury as the respective negative and positive active materials. This latter compound had the advantage over copper oxide in that it enabled a considerably higher E.M.F.—about 1·8 volts—to be obtained; and when any was dissolved by the electrolyte, it did not give rise to injurious local action at the negative, but, on the contrary, was usefully employed in maintaining its amalgamation. Unfortunately its resistance was too high for it to be an efficient depolariser, and it proved unmanageable in practice.

Nickel oxide was the only one named as an alternative to copper oxide in the first of the patents which led up to the Desmazes cell, but in the last of the series it was omitted along with a number of others afterwards suggested, and silver oxide and copper oxide alone were mentioned. Some stress was laid upon nickel oxide in a patent of A. Dun and

F. Hasslacher in 1887, while in one taken out by T. de Michalowsky in 1899 its qualifications are again put forward and methods described for its commercial preparation.

Output of Zinc/Copper Oxide Cells.

The ampere-hour output of the zinc/copper oxide accumulator far exceeds that of the zinc/lead peroxide combination. The reduction of weight effected in the negative electrodes, as compared with those of an ordinary lead cell, is about the same for each; but in the alkaline cell nearly as great a saving can also be made at the positive electrodes, and for very similar reasons. The combining weight of copper (33) is even lower than that of zinc, so comparatively little of the copper oxide active material is required; and the copper support need also be of but slight proportions and weight. Unfortunately, however, the E.M.F. of the combination is very low, only about 0.8 volt, or just one-third that of the zinc/lead peroxide cell, and when, therefore, the total energy or watt-hour output for weight comes to be considered, the two are very much on a par.

The large bulk and weight of the alkaline electrolyte relatively to that of the electrodes is rather striking, but this is due to the latter being of such small dimensions; and if the amount required is compared with the ampere-hour output of the cell, it will not be found to differ to any marked degree from what is necessary in other types of accumulators. This does not hold good though when the watt-hour output is made the standard of comparison, and in that respect the cell is certainly far more bulky, which is a decided disadvantage for many purposes.

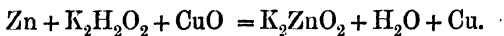
Defects of Zinc/Copper Oxide Cells.

Not only are the inherent weaknesses of the alkaline accumulator just as detrimental to its practical use as those of the zinc/lead peroxide cell, but they are more numerous, because now, in addition to a negative active material normally soluble in the electrolyte, there is a positive active material normally insoluble but passing

over to a soluble condition under the influence of subsidiary reactions, which it is almost impossible to entirely eliminate.

When an electrode of zinc and one of copper surrounded by copper oxide are discharged in a strong solution of an alkaline hydrate, the zinc dissolves up by displacing the hydrogen, which is liberated at the positive electrode, and there reduces the oxide to the metallic state and forms water.

For various practical reasons, potash is found to furnish a more satisfactory electrolyte than soda; and, assuming its use, the chemical changes on discharge may be expressed by one of the two following equations, according to which oxide of copper is present at the positive :—



The first of these applies to a Lalande-Chaperon primary cell, where the black cupric oxide is employed; the second to primary cells of the "Cupron" and the Edison-Lalande types, and to all types which have been re-charged electrically, for on re-charging zinc is again deposited at the negative, while the first and main reaction at the positive is to convert the porous copper into the red sub-oxide Cu_2O . It is, however, extremely difficult to limit the oxidation to this stage, and it is here that the weak point of the electrode is encountered, for, although the sub-oxide is quite insoluble in the electrolyte, directly any cupric oxide or perhaps a still higher oxide forms, it commences to dissolve, passes across to the negative, is reduced there by the zinc, and sets up the usual local action.

It is not at all clear precisely what conditions determine the degree of oxidation, but, generally speaking, the solution of the copper appears to be due to the formation in the electrolyte of peroxidised compounds analogous to those which are produced in acid accumulators on charging, and also gives rise to considerable trouble. Unless some means are adapted for minimising this action and its injurious consequences as much as possible, the copper oxide combination is not a practicable accumulator, as was found to be the case by Lalande, when attempting to reverse

his primary cell. This is the reason for the wrappings of cotton or other vegetable fibre with which the copper oxide has always had to be surrounded, and the envelopes or cells of parchment paper in which the positives have been placed. By their means the colloid or gelatinous hydrated oxide is prevented from escaping to the main body of the electrolyte and the negative electrode, but is kept close to the positive electrode, where it may be reduced again on the discharge. It is the presence of traces of cupric oxide amongst the sub-oxide of positives which have been exposed to the action of the air that renders it so necessary for them to undergo a preliminary discharge after they have been placed in the electrolyte and before they receive their first charging.

The protective coverings of the positives are chiefly directed to localising the cupric compounds; to hinder their formation various precautions must be observed in the working of the cells. The one of most importance is to maintain them at a temperature of about 55°C . during both the discharge and re-charge. It seems that the peroxides which cause the mischief are readily decomposed at this temperature, so they do not form at all or only in very diminished quantity. It is also necessary not to charge at too high a rate nor to continue it to too high a voltage limit.

When zinc dissolves in an alkaline hydrate to form a zincate—a weak compound in which zinc oxide plays the part of a feeble acid radicle—the energy liberated is only about half what it gives in dilute sulphuric acid. This is shown chemically by the fact that zinc alone does not dissolve at all in the cold solution, and electrically by the low E.M.F. furnished when it dissolves in voltaic combination with some depolarising agent. It follows, therefore, that its susceptibility to local action is also very much reduced, and an amalgamated support is not the absolute necessity that it is in an acid electrolyte. Tinned iron has generally proved to be the best material to receive the deposit, and there should then be practically no action between the zinc and the electrolyte on open circuit were it not for the two causes already alluded to, namely, the peroxides in solution and the precipitated copper from the positives. The troubles associated with the negative electrode do not end here, however, and although local action

may be eliminated, there are other causes which tend to spoil the deposit, for it frequently takes the form of a loose grey powder mixed with sub-oxides of zinc, but what these causes are yet remains, like other obscure points connected with the working of the cell, to be satisfactorily explained.

One known cause of irregularity in the zinc deposit is the viscosity or sluggishness of the electrolyte, which so retards the diffusion from one part to another that it gradually separates into strata of different densities, those at the bottom being saturated with dissolved zinc, while those at the top contain very little. This effect is far more pronounced than in any acid electrolyte, and if means are not taken to rectify it, by circulating the electrolyte, endless trouble ensues. Heating the electrolyte is, of course, one method of effecting this purpose, so this procedure really fulfils two different but equally important functions.

Another weak point about the electrolyte is the extreme avidity with which it absorbs carbonic dioxide from the air to form an alkaline carbonate, and unless it is protected in some way its power of dissolving zinc will rapidly diminish.

In view of this formidable array of difficulties to be overcome, it is hardly surprising that for the present the zinc/copper oxide cell seems quite to be put aside. Although not very likely, it may possess latent possibilities yet to be developed, for after all very little is really known about its electro-chemistry, and we are indebted to Schoop for nearly everything that has so far been written on the subject.

Edison's Alkaline Cells.

Edison's name has long been associated with that form of the zinc/copper-oxide combination known as the "Edison-Lelande," and constituting a primary cell capable of giving a large ampere-hour output at a low but constant E.M.F. ; but quite recently he has described two new combinations with alkaline electrolytes which he considers are really reversible and not subject to the defects hitherto attendant upon this type of cell. The first of these, patented in 1900, is a cadmium/copper-oxide combination. In his specification he maintains that the copper-oxide passes into solution on

recharging, because it is too dense and contains particles of imperfectly oxidised metal; and that if it is suitably prepared and sufficiently porous this vital fault will be entirely obviated. With this object in view, carbonate of copper is reduced by hydrogen at as low a temperature as possible, the finely-divided metal then moulded into thin blocks or slabs under slight pressure, converted into black oxide—cupric oxide,

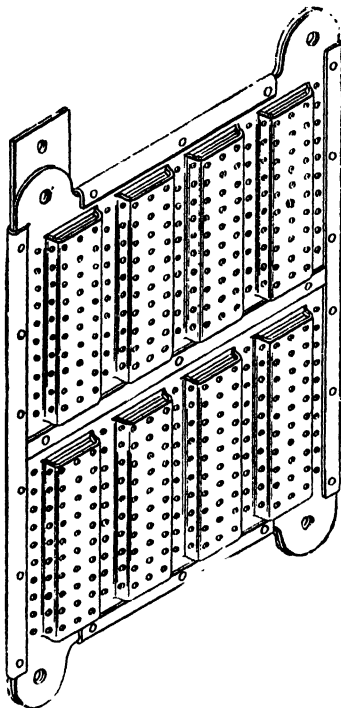


FIG. 128.

CuO—by heating for six to seven hours in a closed chamber at a temperature not exceeding 260°C , and then again reduced, but this time electrolytically, to the metallic state. The blocks are now ready for insertion in the pockets or recesses produced in a thin sheet of perforated nickel or nickel-plated iron by stamping it up. The electrode is shown in Fig. 128. There are no pockets on its other side, which is

presumably covered in with a flat sheet of perforated metal and the two held together by the side ribs and rivets. On first charging, the active material is oxidised up to the red oxide—sub-oxide, Cu_2O —and is then ready for use.

The chief novelty of this cell lies, however, in its negative active material, consisting of finely divided metallic cadmium prepared by deposition upon a platinum wire from a solution of cadmium sulphate. After washing, it is packed into recesses in plates similar to those used for the positives. The metal oxidises upon discharge, but does not then dissolve in the electrolyte, so in this respect it behaves more like a lead negative in an acid solution than a zinc negative in an alkaline one. The electrolyte recommended is a 10 per cent. solution of sodic hydrate.

Early in 1901 Edison filed a second specification which relates to an iron/nickel-oxide combination. The positive active material may be an oxide of either nickel or cobalt, but the former is preferred on account of its lower cost." It is prepared by precipitating the hydrated oxide, which is then dried, powdered, mixed with nearly half its weight of flake graphite, moistened, and packed into a thin case of sheet nickel with perforated sides. The electrodes are now formed as positives for some considerable time, and the nickel-oxide is thereby carried to a higher stage of oxidation and is ready for use. But in this cell, as in the other, it is more especially with regard to the negative active material that a new departure is made. It is prepared from monosulphide of iron mixed with one-fourth its weight of flake graphite, and packed into nickel electrodes similar to those used for the positives. The negatives are then formed in a solution of potassic hydrate by alternate oxidisations and reductions. Sulphur is eliminated as potassium sulphide, and ultimately nothing but finely divided metallic iron is left. Edison states that unless the iron is prepared in this way or from ferric hydrate which has been boiled with water for many hours, it is not susceptible to electrolytic reduction or oxidation to any practical extent. Spongy iron reduced by hydrogen from various iron salts cannot be used on this account. The graphite mixed with the active materials does not take part in the reactions, but is used merely to improve

the conductivity of the mass. On discharge the iron is oxidised, and the nickel oxide partially deoxidised, but only sufficiently to bring it to a lower stage of oxidation, and not enough to reduce it to the metallic state; and as the ultimate reactions of discharge and recharge are simply the transference of oxygen backwards and forwards between the two electrodes, only sufficient electrolyte need be provided to form a conducting medium from one to the other.

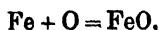
In a third specification, published in England at the beginning of September, 1901, Edison described a number of modifications in the methods of preparing the active materials and constructing the electrodes which were set forth in his previous patent. Ferric oxide is heated to a temperature of 260°C . in a closed chamber and reduced to a mixture, in which ferrous oxide largely predominates, by passing dry hydrogen over it for two or three hours. The chamber is then allowed to cool, but the passage of the gas is maintained for about 15 hours, in order to render the mass—which would otherwise re-oxidise and burn on exposure to the atmosphere—non-pyrophoric. The ferrous oxide is next very carefully and intimately mixed to a stiff paste with one-fourth its weight of flake graphite, dried, and moulded into suitably shaped blocks under a pressure of 300kg. per sq. cm. This constitutes the negative active material.

For the positive active material, nickel hydroxide, $\text{Ni}(\text{HO})_2$, is precipitated from a boiling solution of nickel nitrate by means of magnesium hydroxide. It is then thoroughly washed and dried, treated with dry chlorine to convert it into the hydrated sesquioxide, again washed to remove the nickel chloride, dried, and finally mixed with two-thirds its weight of flake graphite. It appears that the great difficulty with the positive active material is to obtain the nickel hydroxide in such a form that it shall not swell excessively when placed in the alkaline electrolyte, and so put an undue strain upon the electrodes. This is why the hydrated sesquioxide is preferably used and why it must be prepared in the way just described, for Edison states that if obtained by more usual methods which furnish a colloidal hydrate, it expands to an objectionable extent, besides being very troublesome to manipulate on a commercial scale.

The construction of the electrodes is very fully described in the specification, but it is hardly necessary to give the details here. Essentially, an electrode consists of a number of thin strips of consolidated active material, each enclosed in a slight two-part sheath of perforated nickelled steel, which is placed in a corresponding slot in a grid stamped from a thin sheet of the same metal. The electrode is then subjected to hydraulic pressure between suitable dies, which corrugate the faces of the sheaths, and, at the same time, compresses and compels them all to take a firm grip on the containing grid.

In a paper on "The New Edison Storage Battery" read by Dr. A. E. Kennelly before the American Institute of Electrical Engineers in May, 1901,* no reference whatever is made to the cadmium/copper oxide cell, so it may fairly be assumed that it has either not proved so satisfactory as was anticipated, or, at any rate, is distinctly inferior to the iron/nickel oxide combination, and that it is the latter to which Edison pins his faith. Quite apart from its commercial merits and possibilities, the nature of this cell is such as to suggest some interesting points, especially with regard to the use of iron as a storer of energy, which well deserve a little consideration.

Although iron is far cheaper than any other metal, and should yield, weight for weight, a watt-hour output about the same as that of zinc and many times greater than that of lead, it has not hitherto been found possible to employ it in a reversible cell. Its re-deposition from any acid electrolyte in which it is soluble is so uncertain, and its susceptibility to attack by local action so uncontrollable—in spite of its combining energy not being so great as that of zinc—that its use under such conditions seems quite out of the question. In an electrolyte containing free alkali these troubles disappear, for the iron can then only form insoluble compounds, and there is no local action. Edison has been subjected to some criticism for saying there can be no local action because iron cannot decompose water, but the remark appears to be substantially correct. According to the thermo-chemical figures, the E.M.F. due to the oxidation of iron,



* *The Electrician*, Vol. XLVII., p. 266 (June 7, 1901).

is 1.47 volts, while the *minimum* E.M.F. required to electrolyse water is 1.48 volts, so it is hardly likely that iron will effect the transfer of the oxygen except in the presence of something which acts as a depolariser and combines with the liberated hydrogen. On discharge, this is furnished by the oxygen of the nickel-oxide at the positive electrode, but not, of course, on open circuit. It is improbable that the alkali itself reacts with the oxide of iron, or, if it does, the combination is such an exceedingly feeble one that it will contribute next to nothing to the E.M.F.

Because of its energetic union with the acid ions, iron reacts too readily with an acid electrolyte; but the difficulty in an alkaline electrolyte is to get the iron to react at all. Being insoluble in the solution, it must necessarily be used in some porous or finely divided form, and, as already stated, Edison finds that, when prepared by the usual known methods, it is practically unoxidisable. Kennelly further describes this by saying that "it assumes the well-known passive state," evidently alluding to the special conditions under which iron becomes insoluble in and remains unaffected by strong nitric acid; but it is questionable whether this is not to confuse two phenomena which, while superficially alike, are really of a different or even opposing nature, for it is generally believed that the metal is protected from the acid by a thin skin of oxide on its surface. That is to say, the "passive state" of iron is the result of oxidation rather than of inability to oxidise.

The important fact, whose discovery is the essence of Edison's invention, is that, while most forms of iron cannot be oxidised and most salts of iron cannot be electrolytically reduced in an alkaline solution, there are a very few which will reduce to the metallic state and oxidise again with comparative facility. Indeed, he goes so far as to say in one of his patents that probably none other than the two he there names can behave in this way. One of them, the monosulphide, has not been much studied, but the other possesses certain characteristics which long ago caused considerable attention to be devoted to it, and which now suggest the most probable explanation of its special behaviour in the cell. The substance in question is a curious modification of ferric monohydrate,

$\text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$, obtained by boiling ordinary precipitated ferric hydrate, $\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$ or $\text{Fe}(\text{HO})_3$, for many hours. After that treatment it is no longer soluble in strong acids, and although dilute acids dissolve it, they do not form the usual iron compounds, for a gelatinous hydrate is re-precipitated on the addition of concentrated acids and certain salts which generally have no such effect. Moreover, when in solution it altogether fails to respond to some of the most distinctive tests for iron, as, for instance, those with ferrocyanides and sulphocyanides. Having regard to these and other properties, the opinion was formed that it must be an allotropic variety of the normal ferric hydrates, and Mendelejeff believes that it is a polymerised compound of very complex molecular structure.

The distinction between electrolytically active and passive (using the word in Kennelly's sense) materials or the active and passive states of the same material is by no means peculiar to iron and its compounds. In connection with the preparation of his positive active material, Edison speaks of its holding good for nickel and cobalt, and the ordinary lead accumulator provides some well-known examples of the contrast between the two conditions. The lead sulphate formed during the normal working of the cell and the white irreducible sulphate afford the best case of this kind, but the spongy metallic lead of the negatives also appears to be capable of existing in either state.

The general interest which has been taken in Edison's new cell has caused much attention to be given to the possibilities of the oxides of nickel as depolarisers in an alkaline solution. Some notes on the chemistry of these rather obscure substances have recently been published by A. L. Marsh,* who worked at the subject independently of the results of Michalowski and of Edison; and they may be found useful for reference by others undertaking similar investigations. He classifies the oxides into three well-defined compounds and two others of doubtful composition.

1. Nickelous oxide or protoxide of nickel (NiO) is a green powder, turning yellow upon heating. It oxidizes to Ni_2O_3 .

* *Electrical World*, Vol. XXXVIII., p. 136, July 27, 1901.

upon being heated above $350^{\circ}\text{C}.$, but is again converted to NiO upon raising the temperature above $600^{\circ}\text{C}.$

2. Nickelic oxide or sesquioxide of nickel (Ni_2O_3) sometimes, but wrongly, called peroxide of nickel, is a black powder formed by decomposing some salt of nickel, as nickel nitrate or chlorate, by heating to the lowest possible temperature which produces the decomposition. It is also formed by the action of hypochlorites upon nickelous oxide suspended in alkaline solution.

3. Nickelo-nickelic oxide (Ni_3O_4) is a grey, metal-like non-magnetic solid.

4. Nickel suboxide (Ni_2O) is said to exist.

5. Nickel peroxide, supposed by Edison to have the formula NiO_2 and called by him superoxide of nickel, is formed by the action of electrolytic oxygen on nickelic oxide in an alkaline solution. It is thought to be formed by the action of hypochlorites on the hydrated nickelic oxide, $\text{Ni}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. Wicke gives its composition as Ni_4O_7 , and Bayley as Ni_3O_5 . When formed in the wet way a hydrate of the oxide results rather than the simple oxide, but in most cases only the latter need be considered. Nickelic oxide prepared in any way except electrolytically is inert; that is, it produces no E.M.F. when opposed to zinc or cadmium in an alkaline solution. When, however, a current is sent through the solution from the nickelic oxide plate to the cadmium, the couple becomes active, so it is quite probable that the substance of the active nickelic oxide plate is a higher oxidation product. The same remark applies to the oxide when prepared electrolytically, as described above.

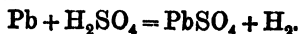
CHAPTER IV.

THE PROPERTIES AND BEHAVIOUR OF LEAD CELLS.

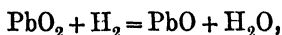
Lead storage cells generate electrical energy by means of chemical reactions taking place between lead, lead peroxide and dilute sulphuric acid—that is, their two active materials and their electrolyte. Although the main lines upon which these reactions proceed have been fairly conclusively ascertained, their exact nature is in many respects very complex and puzzling, and much difference of opinion regarding them still exists. This aspect of the subject is more fully dealt with in the next chapter, but as it is impossible to discuss intelligently the physical behaviour and electrical properties of the cells without at the same time taking some account of the chemical changes with which they are related, a brief outline of them will be given here.

Discharge Reactions.

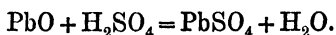
The E.M.F. existing between the terminals of a charged lead cell is due in the main to two causes: one, the affinity of lead for oxygen; the other, the readiness with which lead parts with some of the oxygen combined with it in lead peroxide. It is as if a molecule of oxygen were striving to transfer itself from the positive to the negative: Pb/PbO_2 tending to become PbO/PbO . The actual reactions are, however, more complicated, because the electrolyte, through whose medium the change is effected, itself enters into combination with both active materials. At the negative electrode, lead displaces hydrogen from sulphuric acid and forms lead sulphate.



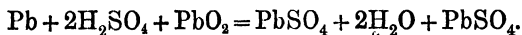
At the positive electrode, the hydrogen thus set free abstracts oxygen from the peroxide to form water.



and the residual lead monoxide reacts with the sulphuric acid, also producing lead sulphate and a second molecule of water.

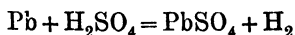


The reactions are divided up in this way to indicate more clearly the affinities at work, and it must not be supposed that they really occur in these stages, but simultaneously, each of equal importance to the normal E.M.F. of the cell; the total result being that at the electrodes Pb/PbO_2 become $\text{PbSO}_4/\text{PbSO}_4$, and in the electrolyte H_2SO_4 is replaced by H_2O .



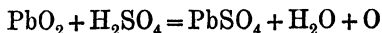
This constitutes what is termed the double sulphation theory of discharge and was first propounded by Gladstone and Tribe in 1882.

There is another way of regarding the discharge reactions which is in some respects more instructive than the orthodox one just given, because it shows how very equally the available chemical energy is divided up between the two electrodes, and not, as is sometimes supposed, contributed almost entirely by one or the other of them. The combining energy of lead is by itself hardly sufficient to displace hydrogen from sulphuric acid when the acid is considerably diluted and its affinity for water has also to be reckoned with. The calculated E.M.F. due to the reaction



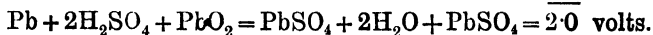
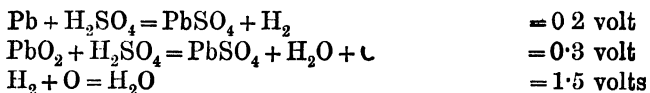
is nearly 0.2 volt, but this does not take into account the polarisation E.M.F. to be overcome before the hydrogen can be liberated in a free gaseous state, and when the lead and acid are pure the spontaneous sulphation and discharge of the active material fortunately does not occur unless the acid is too strong; but the presence of impurities, especially of traces of certain metals electro-negative to lead may just make the difference, and the continuous evolution of gas bubbles from charged negatives on open circuit is a sure sign that local action is proceeding.

On the other hand, lead peroxide maintains but a feeble hold on its second molecule of oxygen. A recognition of this fact may be seen in its employment for lucifers, fireworks and other mixtures where rapid and easy combustion is essential. Indeed, its reaction with dilute sulphuric acid to form lead sulphate and water, and accompanied by the liberation of half its oxygen in accordance with the equation



should afford a resultant E.M.F. of about 0·3 volt, or nearly double that which is available with lead and sulphuric acid; but this notwithstanding, there is no local action unless hot concentrated acid is used, a condition never likely to be realised in practice. The reason is similar to that holding good at the negative, *i.e.*, the nominally surplus energy is in reality not sufficient to overpower the polarisation E.M.F. of oxygen and evolve it as gas, unless re-enforced by special circumstances.

When, however, a circuit is completed between the terminals of the cell, the hydrogen almost liberated at the negative and the oxygen almost liberated at the positive are now enabled to combine to form water, and the E.M.F. of this reaction added to the two others make up the total E.M.F. of discharge.



These numerical values are the roughest of approximations, and apply most nearly to charged cells containing a dilute acid electrolyte of ordinary strength

It need hardly be pointed out that the real composition of the electrolyte is not shown in any of the equations so far given. No cell, of course, contains H_2SO_4 —pure concentrated acid—when charged, nor H_2O —pure water—when discharged. It is generally employed of such a strength and in such quantity as to correspond to about $\text{H}_2\text{SO}_4 + 15\text{H}_2\text{O}$ in a charged cell and $\text{H}_2\text{SO}_4 + 20\text{H}_2\text{O}$ in a discharged cell, but the relative proportions of acid and water

and their range of variation during discharge may differ considerably without affecting the character of the reactions. It is not so generally recognised that, in a similar way, PbSO_4 does not indicate the true nature of the active materials at any normal stage of charge or discharge whatever, for the maximum degree of sulphation to which they attain may be represented by $2\text{Pb} + \text{PbSO}_4$ and $2\text{PbO}_2 + \text{PbSO}_4$ respectively; or, to adopt the more usual phraseology, a large residue of lead and lead peroxide always remains unacted upon at the end of the discharge. Indeed, as applied to the normal products of discharge, the term "lead sulphate" and the formula PbSO_4 simply stand for lead compounds containing varying and indefinite quantities of SO_4 , about whose constitution our present knowledge is extremely vague and meagre. They possess, however, the most important characteristic of being entirely and efficiently broken up again and desulphated on charging, with hardly any expenditure of current beyond what is theoretically required. SO_4 is returned to the electrolyte and Pb and PbO_2 re-formed at the electrodes.

But under certain conditions a compound appears in the active materials which is distinguished by the absence of this property. It can only be reduced or peroxidised with extreme difficulty, if at all, and it may still be found in the fully-charged electrodes; it has, in fact, ceased to form part of the electrolytic circuit, for it is both insoluble and non-conductive. When present in considerable quantities its white colour may easily be recognised, and there is little doubt that it is identical with the ordinary white lead sulphate of the chemist, which really corresponds to the formula PbSO_4 . By reason of its qualities it has variously been termed the "white sulphate," "abnormal sulphate," or "irreducible sulphate," while active material containing it is spoken of as "sulphated." The existence of a normal sulphation which is the fundamental and vital discharge reaction of both active materials, and of an abnormal sulphation which is their evil genius, and almost invariably indicates trouble, past, present or to come, has always proved a most fruitful source for confusion both of terms and ideas, more especially as what constitutes the abnormal

sulphate in the cell is to the chemist the normal one; but until the essential difference between them has been more clearly ascertained it hardly seems advisable to attempt to modify the existing nomenclature.

Electromotive Force of Discharge.

The E.M.F. of a charged lead cell varies with the percentage of sulphuric acid present in the electrolyte, and its values for solutions up to a specific gravity of about 1·300 are shown in Fig. 129.

Curve *a* embodies the determinations by F. Streintz;* curve *b*, those by Gladstone and Hibbert,† but they are both in very close agreement. It will be noticed that within the

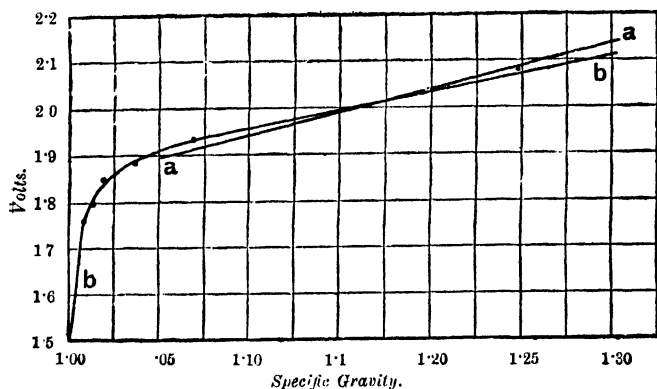


FIG. 129.—Variation of E.M.F. with Strength of Acid.

specific gravity limits 1·050 to 1·300 the rise or fall of E.M.F. is nearly uniform, but this does not hold good with much weaker or stronger acid, because in the former case the nature of the reactions then undergoes a fundamental change, and in the latter case the effects of local action between the spongy lead and the electrolyte begin to come into play and keep down the E.M.F. For these same reasons, however, such solutions cannot be practically employed, and so the E.M.F. of a charged cell—neglecting the initial and transitory increase due to recent charging—will be something between

* *Wiedemann's Annalen*, Vol. XLVI., p. 449, 1892.

† *Journal I.E.E.*, Vol. XXI., p. 420, 1892.

1.9 and 2.1 volts, while for the most usual strength of acid, specific gravity 1.160 to 1.200, it is 2.00 to 2.05 volts.

During the discharge of a cell the sulphation of the active materials and the dilution of the electrolyte go on continuously, and so the E.M.F. is never really constant for two moments together. By using a cell containing a large quantity of solution, and by discharging at a rate which will allow the acid in the pores of the active materials to be always maintained by diffusion at nearly the same strength as that of the main body, the fall of E.M.F. due to weakening of the electrolyte may be rendered practically negligible; but in practice, the time occupied in the discharge is seldom, if ever, so prolonged that considerable local variations in the strength of the acid immediately surrounding the active materials are not eventually set up, no matter how large the total quantity present, and, consequently, the E.M.F. of the cell is more or less reduced by temporary changes resulting from its own discharge.

There are, therefore, three distinct E.M.F.s, or, rather, sets of E.M.F.s, of which account must be taken. First, the true open-circuit E.M.F.s, depending solely on the composition of the active materials and of the electrolyte after perfect uniformity has been restored by diffusion; second, the effective E.M.F.s on closed circuit, which are the true E.M.F.s modified by polarisation; third, the P.D.s on closed circuit, which are the effective E.M.F.s modified by the cell's internal resistance. Reliable observations of the E.M.F.s of the first two kinds are not easily obtained. On stopping the discharge preparatory to measuring the effective E.M.F. that existed on closed circuit, the conditions which determined its value are modified, and it immediately commences to rise, at first very rapidly, but with increasing slowness until a steady E.M.F. is finally reached; so, however quickly a reading may be obtained, it cannot really represent the E.M.F. that was acting on closed circuit; nor, on the other hand, does it indicate the true E.M.F. unless sufficient time has been allowed to elapse for it to become quite constant, which with most cells, most discharge rates, and at most periods of the discharge would mean a considerable interval before the discharge could be resumed. The top curve in Fig. 180

shows the effective E.M.F.s of a cell during the first part of its discharge at a slow and constant rate. It is taken from Ayrton's Paper on "The Working Efficiency of Secondary Cells,"* and every value used for its preparation could itself only be obtained by means of a curve, and not by direct observation. Each time the circuit was broken a number of readings of the E.M.F. were taken at intervals of two seconds, and a prolongation backwards of the curve furnished by these to where it cut the line of zero time—that is, the moment when the discharge actually ceased—gave the required E.M.F. In view of this difficulty of measurement,

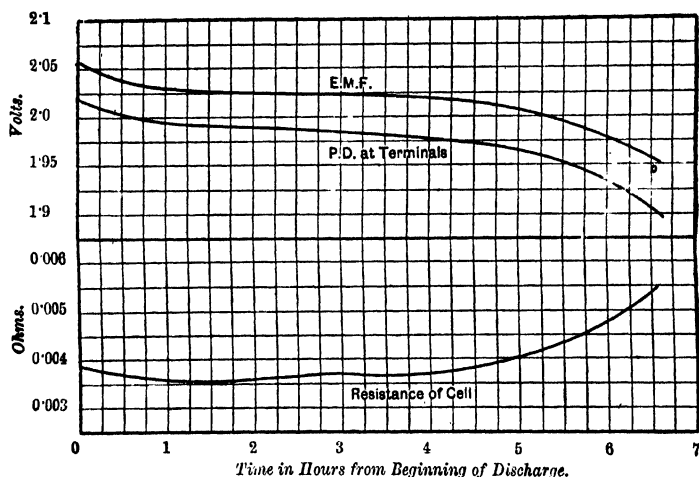


FIG. 130.—Effective E.M.F. and Internal Resistance of Discharge.

it is hardly surprising to find that the P.D.s on closed circuit nearly always have to serve as the index by which a cell's electrical capabilities are gauged and compared; and, although they are no doubt the figures of most practical importance, their relationship to the true and the effective E.M.F.s should not be forgotten, nor that ordinary open-circuit readings are mostly impure values whose significance largely depends on the conditions under which they were determined.

* *Journal I.E.E.*, Vol. XIX, p. 539.

Curves of P.D. are generally expressed in terms of the time in hours from the commencement of the cell's discharge or re-charge, as the case may be, at a constant current; but for purposes of comparison it is often much more instructive to plot them in relation to the ampere-hours put in or taken out.

Initial Fall of Discharge P.D.

Most discharge curves show a rapid initial fall of P.D., resulting from the dissipation of a high but variable and unstable E.M.F. impressed upon the cell towards the end of its previous charge. Whatever its precise causes, it is essentially a polarisation E.M.F. whose value and duration depend largely on the nature of the re-charge as well as on

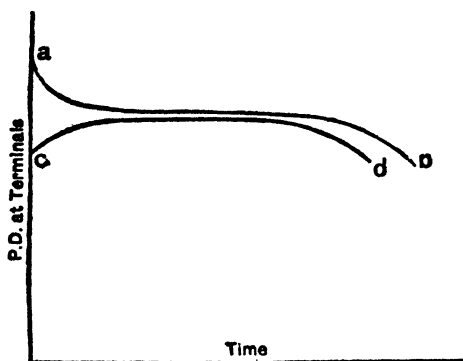


FIG. 131.—Effect of Rest on Initial P.D. of Discharge.

the type of the electrodes and the strength and amount of the electrolyte; but in every case it rapidly decreases on open circuit, and it is only because the discharges from which P.D. curves are constructed almost always follow close upon the re-charge that they so invariably show the effect in its most pronounced form. With pasted plates discharging at slow rates, the first closed circuit reading may be over 2.1 volts, and the P.D. may require an hour or more to sink to its steady value; while with Planté electrodes, discharging fairly fast, not only is the excess voltage less in amount, but it is often dissipated in a very few minutes. Ayrtton has shown that if previous to the discharge of a cell

it has stood on open circuit for a sufficient length of time—some 12 to 16 days in the experiments in question—the first P.D. readings may be below instead of above the normal, and instead of falling as the discharge proceeds, will actually rise for a short time. In Fig. 181, *ab* represents the first portion of the P.D. curve when the discharge commenced immediately the re-charge was finished; *cd* gives the corresponding P.D. curve after a long rest on open circuit. Crompton * has called attention to the somewhat similar behaviour of cells which have not been left on open circuit, but are discharged at high rates. The P.D. falls rapidly during the first few minutes in the usual way, but then it rises for some while before settling down to the steady decrease which continues for the rest of the discharge. The effect is most frequently observed with Planté type

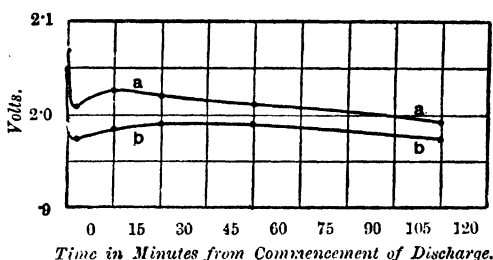


FIG. 132.—Curves showing Initial Rise of P.D. on Discharge.

positives, and two cases noted by the author are shown in Fig. 132. The cell giving curve *a* contained 1.220 acid, and the one from which curve *b* was taken, 1.190 acid, but it does not follow that their slightly differing character was due to this cause. Both the cells were discharged at a 5 to 6-hour rate. The precise reason for these rises of P.D. is obscure, but it is far more likely that they indicate changes in the cell's internal resistance than in its E.M.F.

Curves of Discharge P.D.

Passing to a consideration of the general character of curves of discharge P.D. it may be remarked that they differ far more widely amongst themselves than is usually supposed,

* *Journal I.E.E.*, Vol. XXI., page 452.

and that it is impossible to propound one cut and dried explanation to fit the whole of them. The prime causes which determine the changes of P.D. are few and simple, but according as the construction of the cell and the conditions of the discharge are favourable to one or another of them coming chiefly into play or to their acting together in varying degree, so the nature of the resultant curve may be very different and its immediate causes very complicated. No doubt the disposition of the active materials of the electrodes relatively to their supports is of considerable importance in this respect, but it is quite overshadowed by the other main variables, *i.e.*, the amount and distribution of the electrolyte relatively to the active material, and the rate of discharge. To realise the power these have of modifying the P.D. curve it is necessary to consider a few typical cases or conditions of discharge from amongst the many which may arise. The first is that of an electrolyte maintained of practically uniform composition at all parts of the active materials and with little variation of strength from beginning to end of the discharge. This is, no doubt, a counsel of perfection but the approximate character of its corresponding curve of discharge P.D. is shown by curve *a*, Fig. 133, which was obtained from a cell containing electrodes at an early stage of their formation by Planté's original process and therefore presenting exceedingly thin layers of active material to the action of a large excess of electrolyte. The curve affords two clearly marked characteristics. First, it falls very slowly and uniformly, giving a flat line down to about 1.95 volts, and then it bends sharply over and shoots downwards with great rapidity, indicating that the discharge is completed. The slight slope of P.D. maintained throughout the discharge is partly accounted for by a corresponding fall in the true E.M.F. of the cell, which, in its turn, is determined by the sulphation of the active materials and such slight weakening of the whole body of the electrolyte as may occur, and partly by a small amount of polarisation due to local weakening of the electrolyte which can never be entirely avoided. The reason of the sudden break in the curve is not arrived at so easily. It has been argued that it is caused by a reduction of the cell's E.M.F. resulting from an excessive weakening of the acid solution in the pores of the

active materials; but such an explanation is directly opposed to the test of experience, for the more thoroughly the condi-

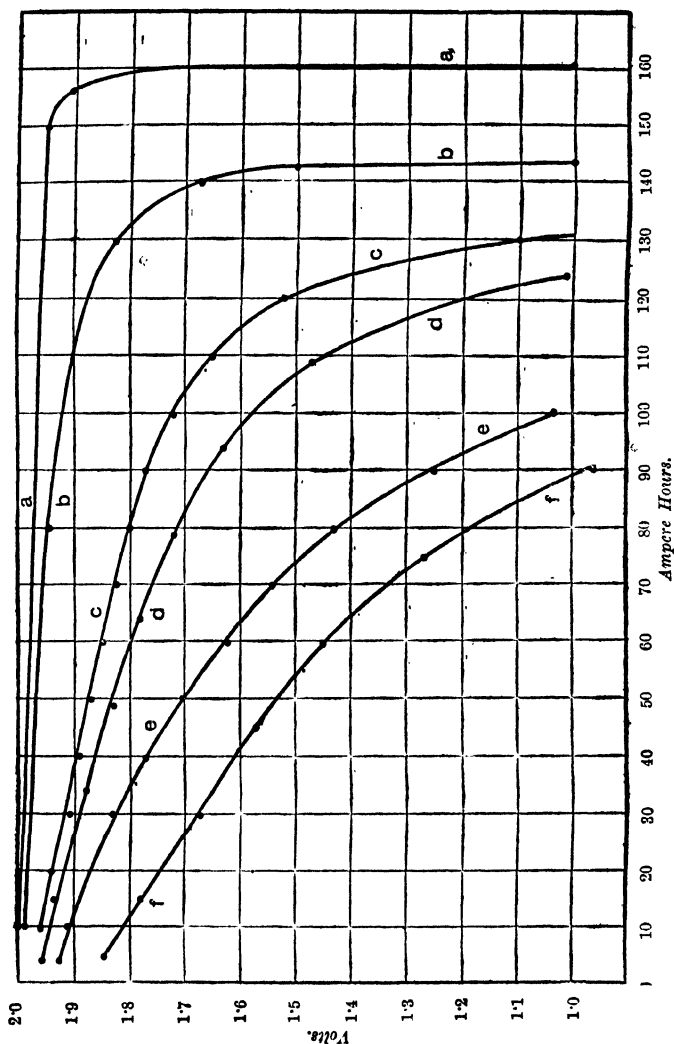


Fig. 133.—Characteristic Curves of Discharge P.D.

tions which could give rise to this state of affairs are avoided, the more pronounced does the bend of the curve become, until

in the extreme case now under consideration, the collapse of the P.D. is quite remarkable in its suddenness.

At first sight there appears to be a most simple and natural explanation, namely, that one or both of the active materials are exhausted, that is to say, not capable of entering into further combination with the electrolyte and therefore unable any longer to maintain an E.M.F. ; but on examination this view also proves to be untenable. However low the discharge P.D. of a cell may have fallen, even if it has been forced down to zero and the cell then left on short circuit for many hours, it begins to recover its E.M.F. immediately the circuit is broken. In some cases there is a practically instantaneous return to the full initial E.M.F. ; in others, more or less time is requisite, and the rise appears to cease somewhat short of the normal, but the recovery is always sufficiently pronounced to indicate clearly and conclusively that the combining affinities of the active materials are not yet saturated. A confirmation of this fact is furnished by the analysis of active materials of discharged cells, for it is now well established and generally accepted that they still contain considerable percentages of lead and lead peroxide even where the conditions have been most favourable for obtaining the largest possible output from them.

If, then, the rapid fall of P.D. at the end of the discharge is not caused by a decrease in the E.M.F. it must result from an increase of the internal resistance ; and if, as the author believes, the active materials of a lead cell suddenly and greatly increase their specific resistance when they have combined with a percentage of SO_4 considerably less than is required for their complete sulphation as understood chemically, this behaviour affords a means by which such a change of internal resistance can be satisfactorily accounted for.

The next condition of discharge to be considered is one in which the strength of the electrolyte falls rapidly and greatly as the discharge proceeds, but at the same rate in every part of the active materials. It is the other extreme to the case just discussed and its characteristic P.D. is illustrated by curves *e* and *f*. These were obtained at rapid but different discharge rates from cells whose electrodes, both positive and negative, contained considerable masses of active material and were only

separated from each other by thin partitions of porous earthenware, the whole arrangement being such that any further supply of acid beyond that already present in the pores of the active materials and the separators could only penetrate very slowly. It follows from this construction that, on discharge, the strength of the electrolyte must fall fairly equally at all parts of the active materials. The portion surrounding their free surfaces will not weaken quite so fast as the remainder, as it has the acid in the pores of the separators to draw upon, and to that extent, therefore, the assumed condition is not strictly complied with; but, considering the small quantity of electrolyte the separators contained and its impeded diffusion, the departure from it will be but slight, and the higher the discharge rate the more will differences of strength due to diffusion from outside sources be minimised. The curves present a marked contrast to curve *a* in every particular. From the commencement of the discharge the P.D. tends steadily downwards, at first in an almost straight line and afterwards with a slight curvature, to 1 volt, when the circuit was broken, although even then the slope of the curves is not much steeper than at the start. There can be no doubt that here we really have an instance in which the variations of discharge P.D. are almost entirely determined by changes in acid strength at the electrodes, the steady fall being the result partly of a diminished E.M.F. as the acid weakens, but more largely of an increase of internal resistance due to the same cause. Having regard to the limited amount of solution taking part in the discharge, it is evident that the active materials never have a chance of reaching that stage of sulphation where their own specific resistance experiences a sudden increase, and all signs of a rapid change in the direction of the discharge curve are consequently absent.

A clear indication of the total difference in the causes which operate to bring about a fall of P.D. in the way shown by curve *a* and those which furnish curves such as *e* and *f*, is afforded by the behaviour of the exhausted cells with regard to "recuperation" and "residual discharges." If the discharge curve has been of the former kind the cell recovers its full E.M.F. almost immediately the circuit is broken, but on again attempting to draw current from it, no matter how

long the interval of rest may have been, the P.D. falls to its previous value with equal rapidity, and no further output or residual discharge can be obtained. But if the cell has afforded a discharge curve of the latter kind the case is reversed. On stopping the discharge, the E.M.F. will, of course, at once increase by the amount previously absorbed in the internal resistance, but the full recovery will be a matter of more or less time, according to the construction of the cell, and may be extremely protracted. When, however, it has taken place, the P.D. can only be pulled down again by a second discharge, which in extreme cases may furnish as large an output as the first and still leave further energy to be drawn out, after appropriate intervals of rest, in subsequent discharges of gradually shortening period. The conclusion is obvious. In the one instance the fall of P.D. is determined by the attainment of some condition which is permanent and cannot be altered except on re-charging, and may, therefore, be fairly ascribed to the active materials. In the other the fall is merely temporary and disappears when sufficient time has been allowed for fresh acid to diffuse into the electrodes; changes in the electrolyte are its immediate cause, and it is only the ultimate limit to the output which rests, as before, with the active materials.

The third condition of discharge is that in which the electrolyte in contact with the free surfaces of the active materials experiences only a small reduction of strength, while the acid in their interior is weakened at a rate and to a degree which vary at different parts. This is the state of affairs that most usually obtains in practice, and its characteristic curve—*b* of Fig. 133—was furnished by a cell with pasted electrodes discharging at a 12 to 15-hour rate; it is, in fact, one taken from Ayrton's Paper already referred to. The variation in the specific gravity of the main body of the electrolyte during the whole of the discharge was roughly from 1.200 to 1.180 which, so far as this change alone is concerned, represents a fall of true E.M.F. of not more than about 0.02 volt. Considering the slow rate of discharge, the electrolyte immediately surrounding the free surfaces of the active material cannot possibly vary through much wider limits, so that as regards acid supply the conditions there are very similar to

those which gave rise to curve *a*. Within the active material, however, the range of variation will be greater, just in proportion as the replenishment of the solution by diffusion becomes less and less, and it will not need to go far below the surface before the state of affairs approximates to that holding good for the whole of the active material in the cell which furnished curves *e* and *f*.

This want of uniformity in the conditions governing the supply of electrolyte to different parts of the active materials introduces a new complication, for the inequalities of acid strength thereby set up mean corresponding differences of E.M.F. and internal resistance, and in order to maintain the same P.D. throughout the electrode, the supply of current energy also becomes unequally distributed. The proportion of the work contributed from each part will depend upon the strength of its surrounding electrolyte, and consequently some portions of the active materials gradually attain to a more advanced stage of sulphation and discharge than others. It is really a very involved case of the distribution of current amongst an infinite number of cells of different and varying E.M.F.s and resistances, all joined in parallel across a common circuit.

The curve follows very nearly the same course as curve *a* for the first half of the discharge and then its slope becomes steeper at a slow but continually increasing rate. This slightly bowed appearance is present throughout the discharge curves of all commercial cells, but the P.D. measurements require to be taken accurately and frequently and to be plotted on a sufficiently large scale to always make it apparent in the earlier stages of the discharge. There is every reason to presume that it originates from the gradual decrease in the porosity of the active materials, which, as they sulphate, expand, and so give rise to more and more imperfect diffusion and an accentuation of all the conditions that tend to increase the rate of fall of P.D. A reference to Fig. 130 will show that, as might be expected, the fall is a result partly of a lowering of the effective E.M.F. and partly of an increase of the internal resistance. After about three-fourths of the discharge have been obtained the downward acceleration of the P.D. rapidly increases until the drop is almost vertical, but

the proportion of the total output over which this change is spread is considerably larger, and consequently the sweep of the curve wider and more gradual than the corresponding terminal portion of curve *a*. This difference is due to the whole of the active material not simultaneously attaining its critical point of change of specific resistance as was previously the case but, for the reasons just now given, reaching it gradually in successive layers.

Curves *c* and *d*, which were furnished by the same cell that gave *e* and *f* but at much slower discharge rates, illustrate

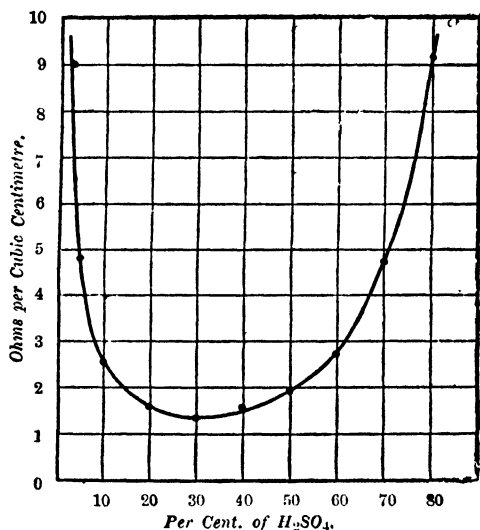


FIG. 134.—Variation of Specific Resistance of Sulphuric Acid.

the variations of P.D. under still other conditions. Here the changes of acid strength must be considerable at all parts of the active material, but much less pronounced at their surface than elsewhere. The initial slope of the curve, due to the weakening of the electrolyte, is so steep that it merges almost imperceptibly into the still more rapid terminal fall of P.D. and it is impossible to say whether this latter is a result of the acid or the active materials having reached their critical point of specific resistance.

The variations in the resistance of solutions of sulphuric acid, according to their degree of dilution, are shown in Figs. 134 and 135, the curves being plotted in terms of percentages of acid and of ohms per cubic centimetre from data obtained by Kohlrausch. Fig. 134 carries the curve to a minimum strength of 2.5 per cent. (specific gravity 1.016) where the resistance has risen to about six times what it was at strengths from 20 to 40 per cent. specific

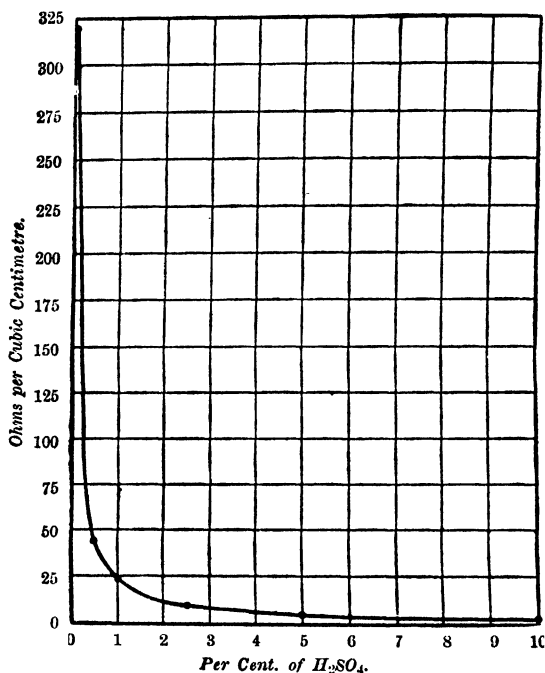


FIG. 135.—Variation of Specific Resistance of Weak Sulphuric Acid.

gravity 1.14 to 1.30). Passing to Fig. 135, in which the curve is plotted on an altogether different scale, the rise of resistance between a 10 and a 2.5 per cent. solution now shows as an almost horizontal line, but from thence the curve makes a sudden bend upwards and the resistance increases over 85 times between 2.5 and 0.05 per cent. It is evident therefore that if, either by reason of the construction of the

cell or the rapidity of the discharge, the strength of the electrolyte round the electrodes is ever pulled down as low as 2 to 3 per cent., the sudden increase of internal resistance there experienced will itself render any further output practically impossible, and it is this stage which is here termed the "critical point" in the dilution of the electrolyte.

It would be possible to continue discussing the variations of discharge P.D. *ad infinitum*, for no two cells are identically the same in this respect; but enough has been said to indicate the main factors which go to determine their character in any particular case, and it will be more profitable to sum up the main conclusions already reached.

Neglecting the transitory polarisation E.M.F. left over from the previous re-charge, there are four electrical causes to which the changes in the discharge P.D. may be ascribed:

First, a fall of E.M.F. due to alterations in the composition of the active materials as their sulphation proceeds; but the variations from this cause are very slight, if indeed they actually exist at all.

Second, an increase of internal resistance due to alterations in the composition of the active materials; such increase is practically negligible up to a certain stage of sulphation, but then it quickly becomes relatively enormous.

Third, a fall of E.M.F. due to alterations in the composition of the electrolyte surrounding the active materials as its desulphation proceeds. The nature of this relationship is shown in Fig. 129.

Fourth, an increase of internal resistance due to alterations in the composition of the electrolyte. As the acid weakens the rise is at first small, then much greater, and then also quickly becomes relatively enormous when nearly all the acid has been abstracted. (See Figs. 134 and 135.)

When discharge curves similar to curve *a*, Fig. 132, are obtained, the first and second causes are chiefly responsible for their character; when the curves are such as *e* and *f* they have been chiefly controlled by the third and fourth causes, but when the curves come intermediate between these extremes, like *b*, *c* and *d*, then all four causes have, in varying degree, combined to produce them. Generally speaking, in proportion as the first two predominate, the curve is flatter in

its initial portion and shorter and steeper at the end, while in proportion as the two last predominate, the curve is steeper at first and flatter afterwards.

The practical physical cause which decides the path of the curve of useful discharge P.D. is the degree of diffusion between the small quantity of electrolyte contained in the pores of the active material and the main body not in actual contact with it. Undoubtedly curve *a* is the ideal curve of discharge, and corresponds to the condition of almost perfect diffusion. It may perhaps be approximated to by some commercial cells containing Planté type electrodes and discharging at very slow rates, but it can only be fully realised under conditions which permit of the current supply being drawn from every part of the active materials with perfect uniformity, and this in itself implies equality of acid strength throughout their substance.

Curves *e* and *f* illustrate as nearly as is possible the condition of no diffusion, which also is one not often arising in commercial cells. This is the reverse of the ideal, for besides the practical disadvantages generally attendant upon an output at such a widely and rapidly varying potential, it gives rise to a state of affairs incompatible with efficiency and injurious to the life of the cell.

Curves *b*, *c* and *d* represent the results of various degrees of imperfect diffusion such as are commonly encountered in practice, but of the three, *b* is pre-eminently the average curve of discharge P.D., for while Planté type electrodes discharging at low rates will generally give curves something between *b* and *a* in character, those from pasted electrodes at high rates will most often come between *b* and *c*.

It is important to remember that the terms "degree of diffusion," "perfect diffusion," and "imperfect diffusion" do not refer to any absolute standard or rate of diffusion, but always to the ratio between the rate at which the active materials are withdrawing acid from the electrolyte immediately surrounding them, and the rate at which further acid is being supplied by diffusion from outside. It follows, then, that whatever the structure of a cell and its electrodes, this ratio may be varied from practically perfect diffusion through every degree of imperfect diffusion to practically no diffusion at all,

solely by altering the rate of discharge ; and, therefore, that any cell is capable of furnishing every variety of characteristic curve of P.D. from *a* to *f*. For instance, it is quite conceivable that a cell whose diffusion was so impeded that it ordinarily gave a curve such as *f* might be discharged so slowly that curve *a* was obtained ; but to accomplish this the discharge would probably have to continue for weeks or months. On the other hand, a cell of very open construction, and with free access of electrolyte to every part of its active materials, may be caused to furnish a curve approximating to *f* by practically short-circuiting it and discharging at an enormous current for a few minutes. Then the rate of diffusion, although fairly sufficient for all ordinary circumstances,

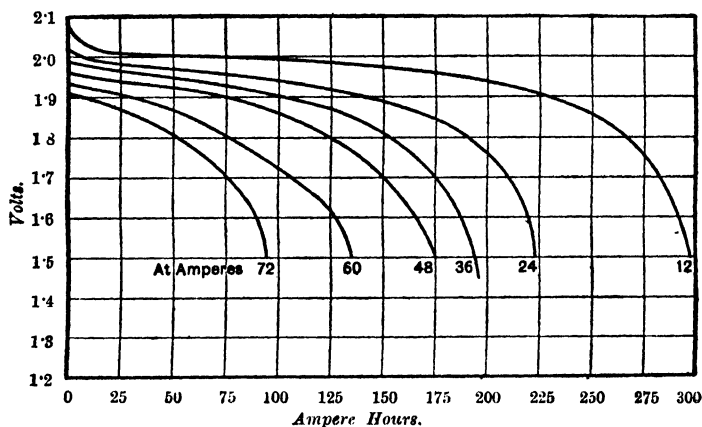


FIG. 136.—Variations of P.D. and Output with Rate of Discharge.

becomes almost negligible compared with the excessively rapid depletion that is going on, and as long as the high current can be maintained, the strength of the electrolyte in direct contact with the active materials falls very nearly as fast as if there were no further supply available. Apart from these extreme cases, the truth of the proposition and the way in which the rate of discharge alters the P.D. curve has long been recognised. For instance, Fig. 136 shows a set of P.D. curves obtained from Crompton-Howell electrodes discharging at different currents.* At the slowest

* *Journal I.E.E.*, Vol. XIX., p. 692.

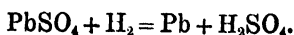
rate the curve is very similar to curve *b*, while at the high rates it is more like *e* and *f*. Thinner electrodes of the same type gave a set of curves which, as a whole, come nearer to *a* and *b* in character; pasted electrodes would give a set nearer *e* and *f*. So the part really played by the structure of the cell and its electrodes is to determine the particular degree of imperfect diffusion that corresponds to any given discharge rate.

The positive and negative electrodes of a cell often differ considerably in their mechanical construction, thickness, quality and disposition of their active materials and their electrical outputs. In such cases the general nature of the curve of discharge P.D. will be a compromise between those the cell would have furnished with electrodes all of the one kind or the other. It is, however, at the fag end of the discharge after the rapid fall of P.D. has set in that such differences show up most markedly, and as lead cells are hardly ever run down below 1·7 volts, the part of the curve below this point is of no practical interest, and has been but little studied. It does not follow that because at, say, 1·5 volts the curve is falling away almost perpendicularly that this continues right down to zero. Sometimes it does, but at others the slope of the curve suddenly becomes less steep, and a further output at low potential can be obtained.

Reactions on Charge.

The chemical changes that take place in a cell on recharging are, in their ultimate effect, chiefly the reversal of those of discharge. The active materials are gradually desulphated and reconverted into lead and lead peroxide, while, in the electrolyte, water is replaced by sulphuric acid. Bearing in mind the qualifications laid down when considering the discharge equations, these processes may be expressed as follows:—

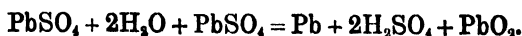
At the negative electrode



At the positive electrode



The sum of the reactions at both electrodes



The E.M.F. required to effect these changes is the same as the E.M.F. they were able to generate when taking place in the reverse direction on discharge—that is, from 1·9 to 2·1 volts according to the strength of the electrolyte—plus a further E.M.F. necessary to overcome the gaseous polarisation. This polarisation consists in the accumulation of oxygen and hydrogen at their respective electrodes. At first, and so long as there is plenty of work to be done in reducing

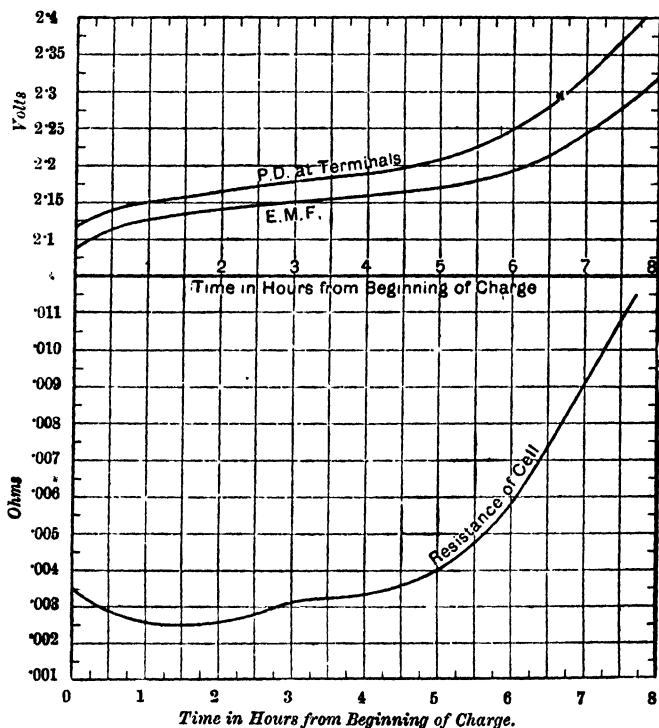


FIG. 137.—Effective E.M.F. and Internal Resistance of Recharge.

and peroxidising the active materials, no gases are liberated, but their concentration increases as the recharge proceeds, and presently an incipient generation commences and soon passes over to the free gassing that indicates desulphation is nearly completed. The consequence is, that the effective E.M.F. of recharge is always distinctly higher than that of

discharge, and the difference between them gets larger when the cell is nearly full, but does not reach its maximum till the charge is completed. Fig. 137 shows the curve of effective E.M.F.s on recharge for the same cell whose discharge curve has already been given in Fig. 130; and to enable a proper comparison to be made between them they are plotted in ampere-hours and put together in Fig. 138—curves *a* and *b*—but with the discharge curve *b* plotted backwards, so that points in a vertical line on each curve correspond to approximately the same composition of the active materials. In this instance, the E.M.F. of recharge exceeds that of discharge by about 0.15 volt at all stages until near the finish, and from there the difference rapidly increases to 0.2 volt at the time of breaking circuit.

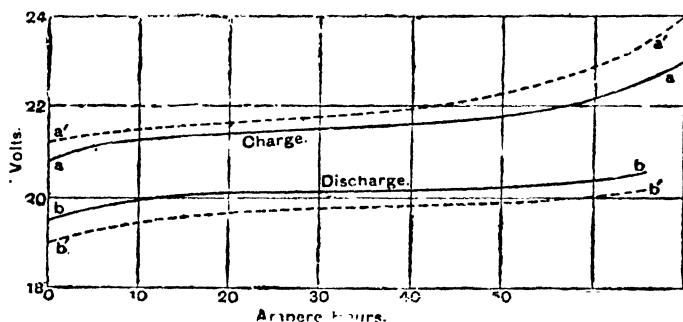
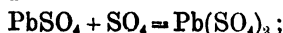
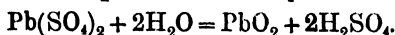


FIG. 138 — E.M.F.s of Discharge and Recharge.

Just as on discharge it is difficult to picture the conversion of lead peroxide into lead sulphate without introducing an imaginary intermediate stage of its reduction to lead monoxide; so, on recharge, it is sometimes easier to consider the re-conversion of sulphate to peroxide in two steps. The first is the direct combination of sulphuric acid with the active material to form lead persulphate,



the second, the immediate reaction of the persulphate with water to produce lead peroxide and sulphuric acid,



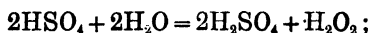
As lead persulphate does appear to resolve itself into peroxide when in contact with water, no particular objection need be

taken to this view of the matter, provided it is clearly recognised that there is no reason to believe that persulphate ever actually exists in the active material as the result of a normal charging reaction.

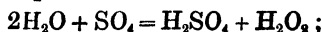
As far as is known, the evolution of hydrogen is the final and only reaction at the negatives after the desulphation of their active material; but, at the positives, the gaseous polarisation towards the end of the recharge forces up the E.M.F. sufficiently to bring about other chemical changes besides the setting free of oxygen. Persulphuric acid and hydrogen peroxide may both make their appearance in the electrolyte, but the relative quantities of each largely depends upon the strength of the acid and other causes which have not as yet been fully investigated. It is generally assumed that persulphuric acid is first formed,



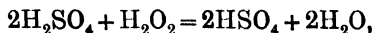
and then reacts with water, giving rise to hydrogen peroxide,



but it may equally well be the other way about, *i.e.*, hydrogen peroxide the direct product,



and afterwards persulphuric acid,



for the reaction between the two compounds appears to be a reversible one and will take place in either direction according to the conditions existing at the time. It is also very probable that the lead peroxide begins to combine with more oxygen than corresponds with the formula PbO_2 , but all these highly oxidised compounds, whether in the electrolyte or the active material, are extremely unstable and they will only go on increasing in quantity until their rate of decomposition equals the rate at which they are produced; after that stage is reached the ultimate reaction at the positive will wholly consist in the liberation of oxygen,



Polarisation E.M.F.s of Recharge.

It is now possible to explain that high but transient and variable E.M.F. which persists for some time after the

recharge has been stopped, and whose effects on the initial P.D. of discharge have already been discussed. Its general nature is shown by the curves in Figs. 139 and 140. The former* gives the E.M.F. for the first few minutes after the cessation of a full charge at a slow rate; the latter† follows the E.M.F. from about the first to the end of the twenty-first hour of open circuit of cells containing four different strengths of electrolyte. The degree of gaseous polarisation that can be maintained at both electrodes, and the degree of super-oxidisation at the positive, will depend upon and increase with the P.D. impressed on the cell; while conversely, the E.M.F. of the cell will be determined by the polarisation and super-oxidisation. Directly the charging circuit is broken, the constraining force which concentrated the gases at the electrodes is removed, their excess is set free, and down goes

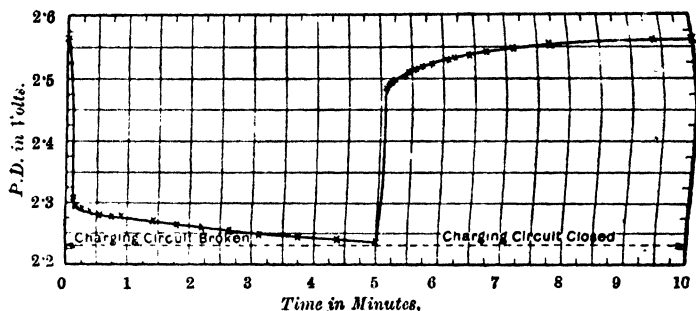


FIG. 139.—Effect of Rest on Polarisation E.M.F. of Recharge.

the E.M.F. The sudden rush of bubbles to the surface may always be observed at the moment of breaking the circuit of a thoroughly charged cell, and the longer the recharge has been prolonged and the higher the P.D. finally reached, so much the more pronounced will this effect be, and the greater the fall of E.M.F. In Fig. 139 there is so nearly instantaneous a drop from close on 2.6 down to 2.3 volts that, as in most cases of polarisation from similar causes, it is hardly distinguishable from an internal resistance loss. It may be remarked in parenthesis that no suggestion of gases occluded

* *Journal I.E.E.*, Vol. XIX., p. 546.

† "Storage Batteries." H. A. Earle. British Association, 1895. *The Electrician*, Vol. XXXV., September 20, 1895.

at the electrodes is intended to be conveyed. This has been proved by direct experiment to be an almost negligible quantity; besides which, gaseous polarisation and occlusion are the result of opposite rather than of similar properties.

The first rush of gas being over, no more is, as a rule, given off by the negatives, unless local action is taking place, but the positives may continue gassing at a gradually diminishing rate for some considerable time. This indicates the breaking up of the unstable superoxidised bodies and gives rise to the slow decrease of E.M.F. shown in the figures. But this decrease is by no means uniform. In Fig. 189, after the sudden drop just dealt with, it continues down-

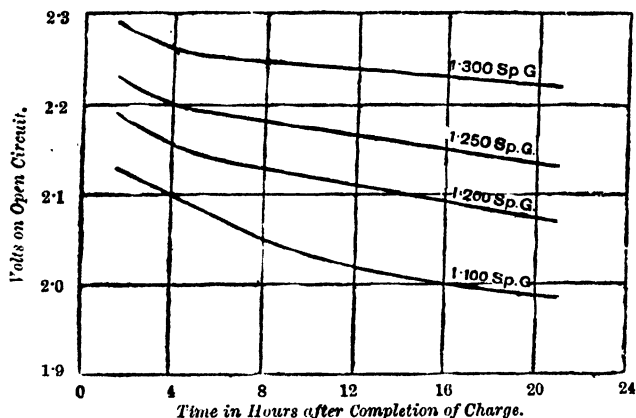


FIG. 140.—Effect of Rest on Polarisation E.M.F. of Recharge.

wards at a rate of about 0.1 volt in 10 minutes. [In this particular experiment the charging circuit was re-made at the end of five minutes. It is interesting to note that the E.M.F. at once rose by about 0.3 volt, the effect of the gaseous polarisation; and then during the next five minutes, as the superoxides again concentrated at the positive, gradually returned to the value at which it stood before the circuit was first broken.] If this were sustained it would not need longer than about half-an-hour for the E.M.F. to reach its normal and permanent value. The rate of fall rapidly diminishes, however, and eventually becomes so slow that it

may be days before it ceases altogether. All the curves in Fig. 140 are still tending steadily downwards at the end of 21 hours. Such behaviour is, however, what might be expected, for the stability of the superoxides will rapidly increase as the proportion of them that remains becomes less, and the last traces may persist indefinitely. At the same time, the slow dissipation of the excess E.M.F. suggests its being due to superoxidisation of the active material rather than of the electrolyte. In the latter case the products would soon be greatly diluted by diffusion into the bulk of the solution in the cell, and diminished by reduction at the negative electrode; and experiments on the addition to the electrolyte of small quantities of persulphuric acid in the form of persulphates do not indicate that it has much effect on the E.M.F.

The curves in Fig. 140 show that for any given time on open circuit, the fall of E.M.F. increases with the dilution of the electrolyte. This again is in accordance with our general knowledge of the highly oxidized bodies, for the stronger the acid—within the limits covered by the curves—the more freely and readily are they formed, and the less easily do they undergo spontaneous decomposition. If a positive plate fully charged in strong acid is removed to a vessel containing water or very weak acid, a considerable evolution of gas from its surfaces will go on for some time.

Besides the gaseous polarisation there is a second cause of polarisation which also goes to increase the recharge E.M.F. This is the strengthening of the electrolyte immediately surrounding the active material by the transfer of SO_4 from the one to the other faster than it can be removed by diffusion. It is the counterpart of the weakening of the electrolyte on discharge by the reverse action, and may therefore be practically eliminated, or largely reduced by employing thin layers of active material with free access of electrolyte and low charging rates. It is this liquid polarisation which causes the rise of E.M.F. during the earlier part of the recharge when the gaseous polarisation is a practically constant quantity. The effects of the various polarisations may be compared by referring to Fig. 138, curves *a* and *b*. The downward slope of the curve of discharge (reading from right

to left) is determined by polarisation due to weakening of the electrolyte round the electrodes; the upward slope on recharge by the strengthening of the electrolyte; and the difference of E.M.F. between the two curves by the gaseous polarisation. The latter, as has already been pointed out, undergoes a considerable increase towards the end of the recharge and accounts for the increased steepness of the curve at that stage. When, as in the experiments from which the curves were constructed, the recharge follows immediately on the discharge and both are effected at about the same current rate, the excess E.M.F. of recharge cannot be due to the liquid polarisation because this is occupied the whole time in cancelling the weakness of the electrolyte produced by the discharge. Only when as many ampere-hours have been put into the cell as were taken out, will this be completely accomplished, while beyond that point there will be very little SO_4 left in the active materials, and so the strengthening of the electrolyte will cease at the negatives and will be largely diminished at the positives. If, on the other hand, time is allowed between the discharge and recharge for the strength of the acid round the electrodes to be partially or fully restored by diffusion, there will then be a real accumulation of acid in the active materials on recharge, and the E.M.F. will be increased by the sum of the two polarisations; but although the curve will now read higher throughout, its slope will not be altered.

Curves of Recharge P.D.

Curves of recharge P.D. vary just as widely in character as do those of discharge, but the causes of their differences have not been nearly so thoroughly examined. Recharging is sometimes effected at constant potential, which consists in maintaining at the terminals of the cell from the very commencement the maximum P.D. necessary to complete the charge; and in such cases there is no curve of P.D., or rather, it becomes a horizontal line throughout. This procedure has the advantage that the bulk of the recharge can be got into a battery exceedingly quickly, for there is at first a large rush of current which rapidly diminishes as the back E.M.F. rises. It is further discussed on page 180, and a curve of recharge

current is also given (Fig. 144). The usual method of charging, however, is at constant current, and under these conditions the ideal curve of recharge P.D. should describe a straight line not much above 2.1 volts all the while the electrodes are being desulphated, and then, directly that process is completed, rise abruptly to 2.5 volts or more by reason of the increase of E.M.E. and internal resistance due to the gaseous polarisation. The chief difference between the recharge curves of effective E.M.F. and of P.D. is that in the latter the end rise is more rapid and much higher because of the large increase of internal resistance that then occurs as

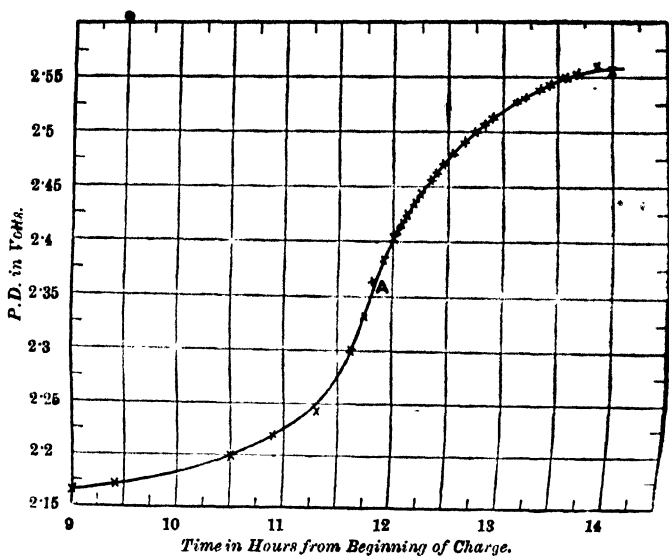


FIG. 141.—Rise of P.D. at End of Recharge.

may be seen by reference to Fig. 137. In practice, owing to the concentration of acid at the electrodes, the P.D. is on the rise throughout the recharge; but, on the other hand, the end rise of P.D. is always more or less gradual, for the desulphation is not finished simultaneously at all parts of the active materials. If the P.D. curve goes up very steeply at the commencement, it may merge almost imperceptibly into the final rise, but this will only occur under the influence of high charging rates or in cells where the circulation of the electrolyte

is exceptionally impeded, and it is unusual not to be able to detect some signs of the change of slope. Fig. 141 gives part of a recharge curve, in which the end rise of P.D. is well marked. After nine hours' charging, the P.D. is still only 2.17 volts, but it then increases to 2.4 volts in the next three hours, and to 2.55 volts in another hour and a-half. In this particular curve the rise of P.D. is most rapid at about 2.35 volts; beyond that point it gradually becomes slower, and has almost ceased when a P.D. of 2.55 volts is reached. Fig. 142 shows the recharge curve of the same cell whose discharge P.D. was given in Fig. 133, curve *b*. At the ninth hour the P.D. is about the same as in Fig. 141, but the subsequent rise is not nearly so rapid, five and a-half hours being required to attain to 2.4 volts, which, in this case, was the limiting value. Probably the only sure method of

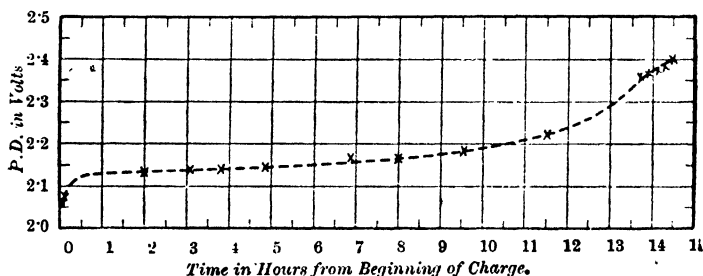


FIG. 142.—Curve of Recharge P.D.

affecting the entire desulphation of the active materials is to continue the recharge until the P.D. has attained its maximum, irrespective of what its actual value may be, for that depends on the construction of the cell, strength of the electrolyte, impressed E.M.F., current density, and other conditions. It may sometimes be forced up to 3 volts, but that is unusually high, and it seldom goes above that figure. Such a course would, however, take too long a time and involve too large a waste of energy in useless gassing, so the recharge is generally stopped at some P.D. at which the desulphation may be considered as approximately complete. This limit must be fixed on its merits according to the type of cell and conditions of working, but it is usually something between 2.4 and 2.7 volts. A somewhat similar decision has

to be made when recharging at constant P.D. instead of at constant current. The decrease of current strength due to the increasing back E.M.F. of the cell is so slow towards the finish that it would require an infinite time to fall to zero, and the recharge is discontinued when it has dropped to some definite amount.

Capacity and Output.

The absolute capacity of a cell in terms either of electrical energy or electricity can only be measured by the watt-hours or ampere-hours it gives out when completely discharged—that is to say when the discharge is continued until the E.M.F. is exhausted. Theoretically and chemically considered, the capacity should be some definite quantity for every cell, determined and limited only by the amounts of active materials and electrolyte it contains. Knowing these and the nature of the discharge reactions, the possible ampere-hours can easily be calculated; and then, multiplying by the true open-circuit E.M.F. of the combination gives the maximum watt-hours. If, for instance, both Pb and PbO_2 are converted into PbO or PbSO_4 on discharge, a cell should yield 100 ampere-hours for every 0.81 lb. of Pb and 0.975 lb. of PbO_2 present. The watt-hour capacity would depend upon the strength and amount of the electrolyte, but, presuming a large excess of acid of 1.170 specific gravity, it should be just double the ampere-hours, for the true E.M.F. of this combination is found by experiment to be 2 volts.

Calculations such as these are, however, based on the assumption that the whole of the energy due to chemical combination in the cell can be realised electrically in the external circuit, which is of course impossible. Owing to internal resistance and polarisation, some of the energy is directly converted into heat in the cell itself, and the loss from both these causes takes the form of a proportionate reduction of the E.M.F. or, what comes to the same thing, a lowering of the terminal P.D. on closed circuit. These internal losses increase as the discharge proceeds, and if it is continued for a sufficient length of time they will eventually absorb so large a percentage of the total energy generated that hardly any is left for the external circuit, and the P.D.

of the cell falls practically to zero. In this way the possible watt-hour output of the cell is greatly diminished, for instead of being twice its ampere-hour output, the multiplier can only be the average voltage obtained by integrating the curve of discharge P.D., and for any given cell the higher the discharge rate the lower will the figure work out. Strictly speaking, a fall of voltage cannot affect the ampere-hour output; but long before the active materials have furnished their theoretically possible capacity, the P.D. has become such a negligible quantity that it can only maintain an infinitesimal current even on short circuit, and an infinite time would be needed to carry their discharge to that stage of full sulphation at which their combining affinities are satisfied and the E.M.F. (as distinct from the P.D.) ceases to exist. In other words, it is not practicable to ever completely discharge a lead cell, and consequently it never yields the ampere-hours that might be expected.

We have already seen that on discharge the P.D. seldom falls uniformly from beginning to end, but, on the contrary, for certain ideal cells, or at extremely slow current rates, remains nearly constant throughout the discharge, and then drops almost instantaneously to zero (*see curve a*, Fig. 133). In such a case, the whole of the practically available energy may be said to have been realised by the time the P.D. has reached 1·8 volts, and a discharge down to this limit represents the full working capacity of the cell. This, however, is the exception. In practice, a far from negligible remnant can generally be extracted at lower potentials, while with some types of cell or the rapid rates at which accumulators are nowadays so often discharged, the ampere-hours not utilised below 1·8 volts may easily exceed those actually withdrawn. In fact, as an inspection of the curves in Figs. 133 and 136 will at once show, the proportion of the total output realised before a P.D. of 1·8 volts—or any other selected voltage—is attained varies with the rate of discharge and the nature of the cell. Experience has conclusively proved, however, that it is most detrimental to the durability and general efficacy of lead cells to discharge them down to too low a P.D., irrespective of how small a percentage of their maximum output has been obtained from them, and so it has come about that

"capacity" is practically defined as that output which a cell will give at P.D.s above some predetermined limit, and the remainder is ignored. This limit is nearly always placed somewhere between 1.9 and 1.7 volts, and is most often fixed at 1.8 volts.

It is most important to remember that in terms of this definition, capacity corresponds neither to what a cell should give out theoretically nor can give out practically, but is merely an empirical and variable fraction of either of these quantities, whose exact amount depends on other properties to which it is not necessarily related in any degree. Thus, by way of a *reducto ad absurdum* illustration, any cell, no matter how large, might have its "capacity" gradually lessened until it vanished altogether by shifting its electrodes further and further apart, for eventually a point would be reached where the P.D. was below 1.8 volts, even on first closing the discharge circuit; or precisely the same result could be arrived at by keeping the electrodes fixed, but sufficiently increasing the rate of discharge. A great confusion of ideas has resulted from the retention of a word which means "the power of containing," and is invariably associated in one's mind with an attribute of definite magnitude, such as cubical contents, to describe something which is very variable and can only be construed as capacity by a violent distortion of that term from its normal sense. It is in every way preferable to always substitute "output," when speaking of discharges obtained under working conditions, and to reserve "capacity" for that quantity which can be realised in theory only but which we have to talk about, even though it cannot actually be measured. In consequence of not making some such distinction, all variations of output or nominal capacity are frequently ascribed to alterations of real capacity, and an altogether wrong idea is formed of their true causes and what goes on in the cell.

The only circumstance which can bring about a change of real capacity is a decrease or increase in the amounts of the effective active materials. They may, for instance, experience some obscure change of constitution by which they lose their power of undergoing electrolytic reduction and oxidation, and cease, therefore, to be *active* materials. Abnormal

sulphation is the most usual action of this kind, but negative active material often alters in some other way as well, with similar results. The active materials may also pass out of the electrolytic circuit and become inactive by loss of contact with their supports ; and the effect would be much the same whether they are merely loosened but retain their position on the electrode, or whether they are entirely detached and fall to the bottom of the cell. Reduction of capacity is generally permanent, but it may sometimes be partially restored by special treatment. A real increase of capacity may also take place from the conversion of the positive metallic support into peroxide active material by local action.

Output is, in the first instance, entirely limited by the extent to which the dissipation of energy goes on in the internal circuit, for to say that the discharge of a cell capable of giving a true open-circuit E.M.F. of 2 volts shall cease on the attainment of a P.D. of 1.8 volts is to say that when 10 per cent. of the total energy of chemical combination is being lost in this way, the capacity shall not be further drawn upon. Everything, therefore, that can affect the internal resistance or polarisation will also affect the output, and it is in this way that it ultimately becomes subject to the influence of an innumerable variety of minor causes. Inequalities and variations in the strength of the electrolyte and its freedom of circulation in the active materials must necessarily have a direct effect upon the output, as also must any alteration in the conductivity between the active materials and their supports. Not only can the output of a cell change quite independently of its capacity, but occasionally the latter can vary without making much difference to the output, for electrodes containing large masses of active material will sometimes shed a considerable proportion of it, and still give nearly as good a discharge as before. Usually, however, it is the other way about. For instance, abnormal sulphation representing an insignificant loss of capacity, may indirectly produce a considerable reduction of output by choking up the pores of the active materials and impeding diffusion ; and, if, as is often the case, the sulphate forms a thin but dense film over the free surfaces of the active materials, the decrease of the output will be still more pronounced. It is very probable

that the restoration of the output of badly sulphated cells by prolonged charging is chiefly due to the actual removal of the sulphate through the vigorous gassing that goes on, and not to its electrolytic reduction; and that the real result is not an increase of capacity but a lessening of internal resistance and polarisation.

If a cell has not been thoroughly desulphated on the previous recharge, or if it has been partially discharged by leakage or local action while standing on open-circuit between the recharge and the discharge, its output will, of course, be temporarily diminished, but in such cases the capacity is unchanged, unless any formation of irreducible sulphate has taken place.

In the early days of commercial lead cells they were listed with a single ampere-hour capacity, perhaps because it was thought that even if they did not always yield this output at least they ought to do so; and it was some ten years or more before it began to be generally recognised that output must alter with the rate of discharge. At the present time the true condition of affairs is better understood, and no statement of "capacity" unaccompanied by the rate at which it can be obtained is considered of any value; while, more often than not, the P.D. at which the discharge terminated is also required. There is no law connecting output and rate of discharge, for the relationship varies with every different make of cell, but the best of them do not, at a three-hour rate, give more than two-thirds to three-quarters of their output on a nine to twelve-hour rate; while if discharged in one hour it is only about one-half or even less.

One of the most important results of Ayrton's investigations, to which repeated reference has already been made, was the experimental proof that even with a fixed current rate and P.D. limit, the output of a cell is a very variable quantity and is influenced by every discharge, recharge or rest on open circuit that it undergoes; in fact, by its whole previous history. Only by putting the cells through exactly the same cycle of discharges and recharges continuously following each other a good many times could they be brought to give a uniform output, and directly the cycle was in any way interrupted or altered the output also varied. If output and capacity were

one and the same thing this behaviour would be inexplicable, but having regard to the nature and variety of the causes which affect the output it is inevitable, for every modification of the conditions must bring some one or other of them into play. It was indicated in the Paper that the variations of capacity might only be apparent and could also be explained in terms of changes of internal resistance.

From a practical point of view Ayrton overproved his case. It would be rather disastrous if, under ordinary working conditions, the output of a cell was as easily reduced by adverse usage as in his experiments, for in that event half the batteries installed would be rendered useless within a 'twelvemonth. He had, however, brought the output to such an abnormally high but unstable pitch, by the special procedure to which the cells were subjected that it was quite exceptionally sensitive to treatment which would affect it very slightly in a usual way.

Influence of Method of Recharge upon Output.

A very good example of the difference between output and capacity is afforded by an investigation made by Messrs. Cohen and Donaldson into the effects of charging lead cells

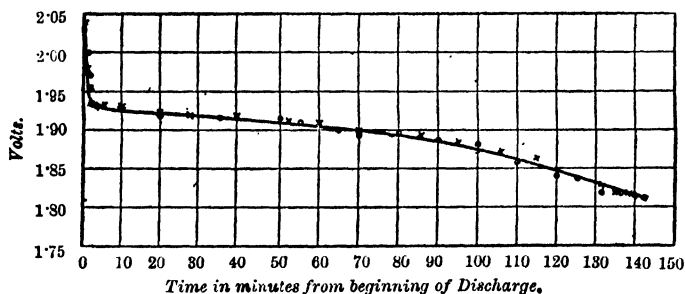


FIG. 143.—Curve of Discharge at Constant Current after Recharge at Constant P.D.

at constant potential instead of at constant current. Their results were published in a Paper read before the British Association in 1893.* The chief object of the experiments was to ascertain how it affected the output and efficiency of the

* *The Electrician* Vol. XLI., p. 674, Sept. 16, 1898.

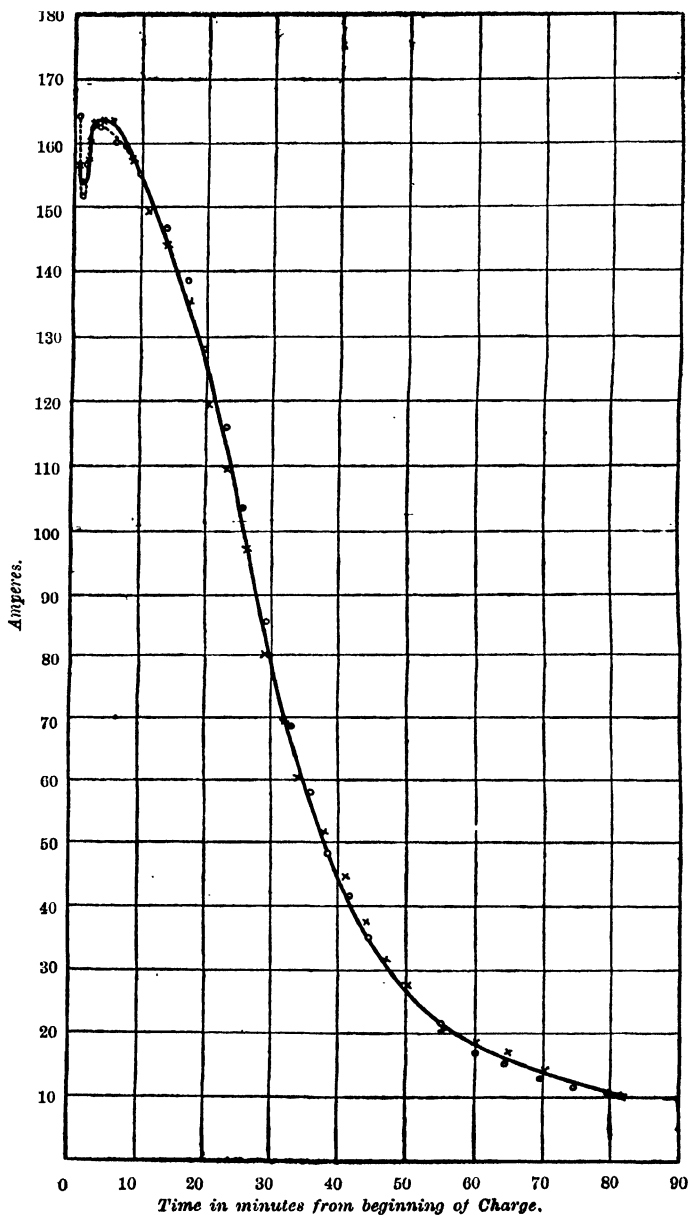


Fig. 144. —Curve of Current during a Recharge at Constant P.D.

cells. A Tudor cell was taken through a series of discharges down to 1.815 volts at a constant current of 36 amperes, and recharges at a constant P.D. of 2.508 volts until the current fell to 10 amperes. When the cell had reached a steady state, in which substantially the same results were obtained time after time, its output was 86 ampere-hours and 163 watt-hours. Fig. 143 gives the curve of discharge P.D., and Fig. 144 that of recharge current. The cell was next put through another series of discharges at a current of 36 amperes, as before, but with recharges at a constant current of 20 amperes, terminating on the P.D. reaching 2.58 volts. The output was now only 25.65 ampere-hours and 123 watt-hour—that is to say, they had both diminished by about 25 per cent. The

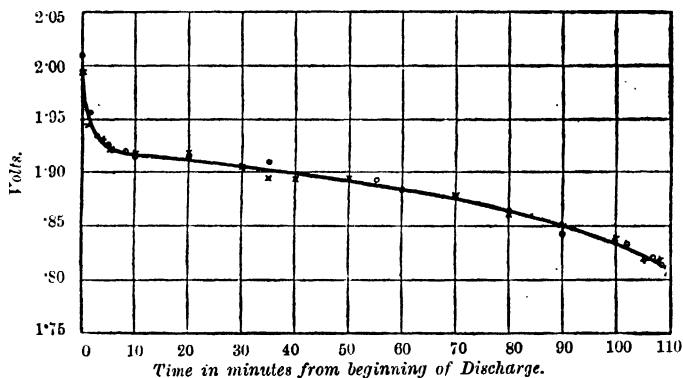


FIG. 145.—Curve of Discharge P.D. after Recharge at Constant Current.

curves of discharge and recharge P.D. are given in Figs. 145 and 146. At first sight it seemed that such a big difference in the results must at any rate be partially due to a loss of true capacity, and to definitely settle this point the cell was again subjected to a cycle of constant P.D. recharges, but it gave practically the same outputs as before, showing that no such change had taken place. On carefully comparing the two discharge curves, Figs. 143 and 145, it will be found that from about 1.92 volts down to the end of the discharge their time falls of P.D. are approximately equal, but that whereas after a recharge at constant current the P.D. drops to 1.92 volts in about 10 minutes, after a recharge at constant P.D. the same drop is spread over nearly 50 minutes. It is

this extra output near the commencement of the discharge, of a little over 20 ampere-hours at a little under 2 volts, amounting in all to 40 watts, which has to be accounted for. Making the fair assumption that whichever method was adopted the active materials were about equally desulphated at the end of the recharge, the only difference that can exist in the cell at the beginning of the respective discharges will be in the strength and distribution of the acid in the electrolyte. In the one case the recharge was completed in 206 minutes; in the other it only took 82 minutes, and in that time, owing to the increased output on discharge, about 33 per cent. more H_2SO_4 was re-formed. On recharge at constant potential, therefore, the acid was liberated con-

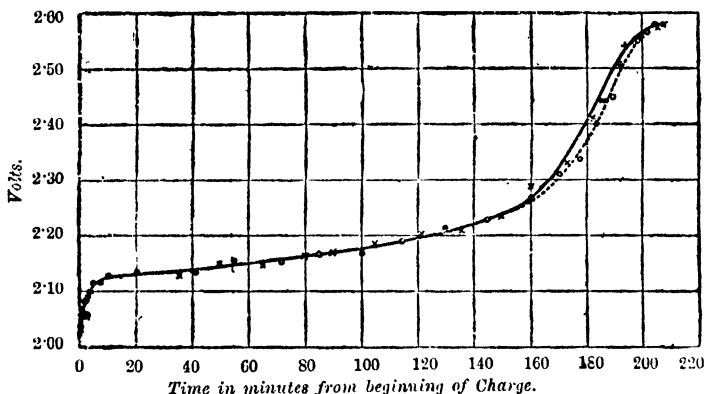


FIG. 146.—Curve of P.D. during a Recharge at Constant Current.

siderably over three times faster than at constant current, and its increased concentration that must ensue round the electrodes appears to afford a reasonable explanation of the larger output; for, at the high rate of discharge being used, the fall of P.D. will be determined chiefly by exhaustion of the electrolyte, and not by the advanced stage of sulphation of the active materials.

Influence of Temperature upon Output.

It has long been known, as a matter of practice, that the output of a battery attains its maximum at a high temperature and may be very distinctly reduced in extremely cold

weather. In 1892, Gladstone and Hibbert* described a laboratory experiment with a small cell whose output was increased some 40 to 50 per cent. at a temperature $15^{\circ}\text{C}.$ to $20^{\circ}\text{C}.$ above the ordinary. Quite recently, however, Heim† has made an investigation of the effects of a change of temperature upon the output of commercial cells which has yielded some remarkable results. Amongst others, a cell which at a temperature of $14^{\circ}\text{C}.$ gave an output of 71 ampere-hours when discharged down to a 1.8 volt limit at a 20 ampere rate, furnished 128 ampere-hours when the temperature was raised to $45^{\circ}\text{C}.$, an increase of 80 per cent; while at a 32 ampere rate the output increased from 53 to 112 ampere-hours, which is more than double, being 111 per cent. (see Figs. 147 and 148.) The output of larger cells discharging at

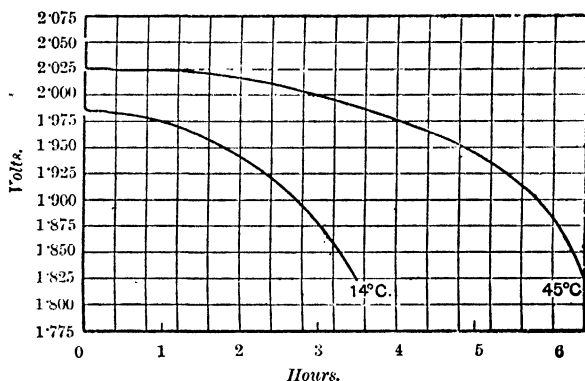


FIG. 147.—Effect of Temperature on Discharge P.D.

a 140 ampere rate, rose from 386 to 785 ampere hours—about 90 per cent.—under very similar treatment. After these figures it is not surprising to find that a cell charged at $15^{\circ}\text{C}.$ and discharged at $45^{\circ}\text{C}.$ gave out about 50 per cent. more electricity than had been put into it, or that when these temperatures were reversed the yield was only just over 50 per cent. of what it had received.

Nothing could emphasise more clearly how large a store of energy is left untapped when discharging at high rates, even

* *Journal I.E.E.*, Vol. XXI., p. 441.

† *The Electrician*, Vol. XLVIII., p. 55, November 1, 1901.

with Planté type positives such as were used in these experiments; nor how much the output may depend on the distribution of the electrolyte rather than the composition of the active materials. What holds good in these extreme cases applies of course, in lesser degree, to the more ordinary variations occurring in every day use.

These experiments of Heim's attracted a good deal of attention and gave rise to some rather wild talk about lead cells acting as heat engines; the idea being that the increased output at higher temperatures is due to a direct conversion of heat into electricity. Such a view is, however, quite untenable, for if the cells really behaved in that way their E.M.F.

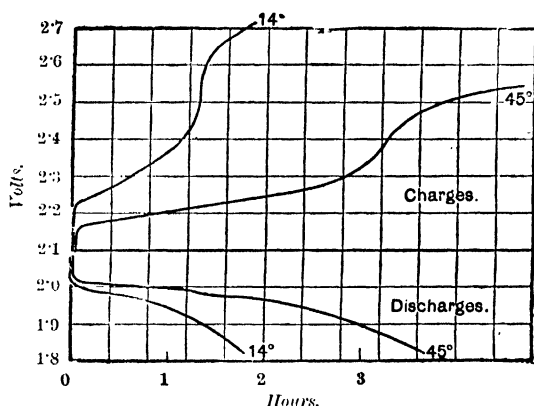


FIG. 148.—Heim's Experiments on the Variation of Output with Temperature.

would be subject to a large positive temperature coefficient—that is to say, it would rise rapidly on heating; whereas it has been clearly established that the variations are exceptionally small for a galvanic element, and their effect on the output is practically negligible. Certainly the average P.D. of discharge increases with temperature, but that is an entirely different matter.

Some further light has been thrown on the relations of output to temperature in a later research by C. Liagre.* He discharged a cell fitted with formed positives and negatives

* *L'Éclairage Electrique*, Vol. XXIX., p. 150, November 2, 1901.

(d'Arsonval-Vaugeois type) at a number of different rates, and for each rate at a number of different temperatures. Curves A, B, C, D and E (Fig. 149) show the discharge P.D. for temperatures of 20°, 27°, 40°, 50° and 70°C. respectively

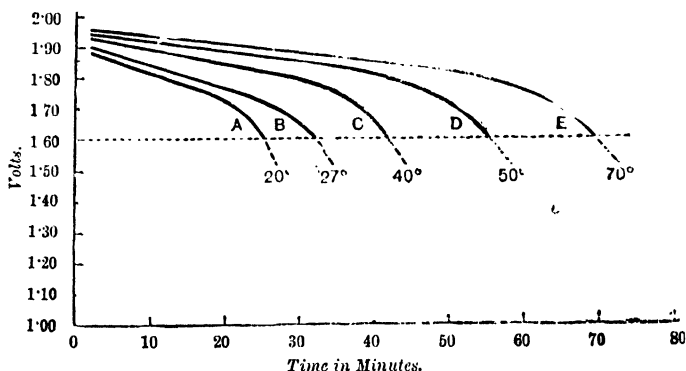


FIG. 149.—Curves of Discharge P.D. at Different Temperatures.
Current rate about 180 amperes.

at a current of about 180 amperes. Fig. 150 gives similar curves at 16°, 32°, 40° and 50°C. for a discharge rate of 25 amperes. Between these two extremes of current several other sets of curves were obtained, and the curves showing

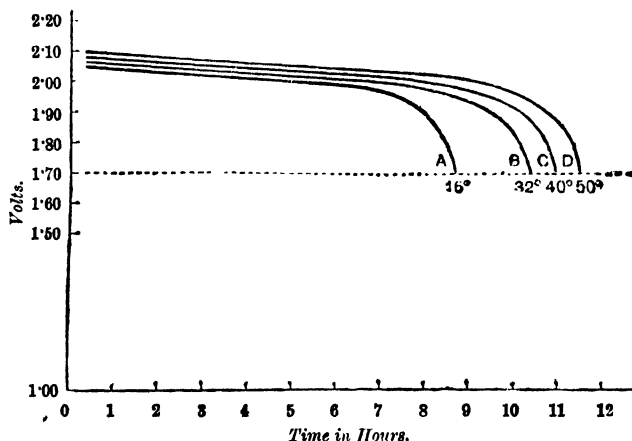


FIG. 150.—Curves of Discharge P.D. at Different Temperatures.
Current rate 25 amperes

the variations of output with temperature for each set are all embodied in Fig. 151.

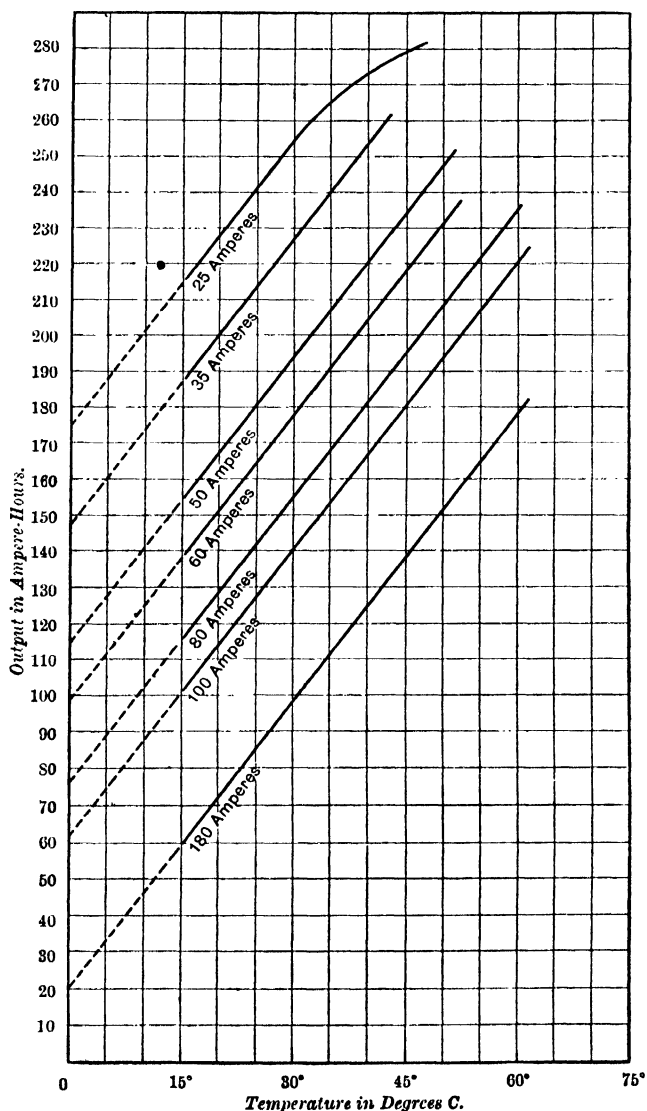


FIG. 151.—Variation of Output with Temperature at Different Discharge rates.

It will be observed that, with one exception, each of these curves is a straight line and they are all parallel; so, within the limits of temperature and rate of discharge covered by the experiments, the increase of output with temperature is perfectly uniform, and the rate of increase is the same for all

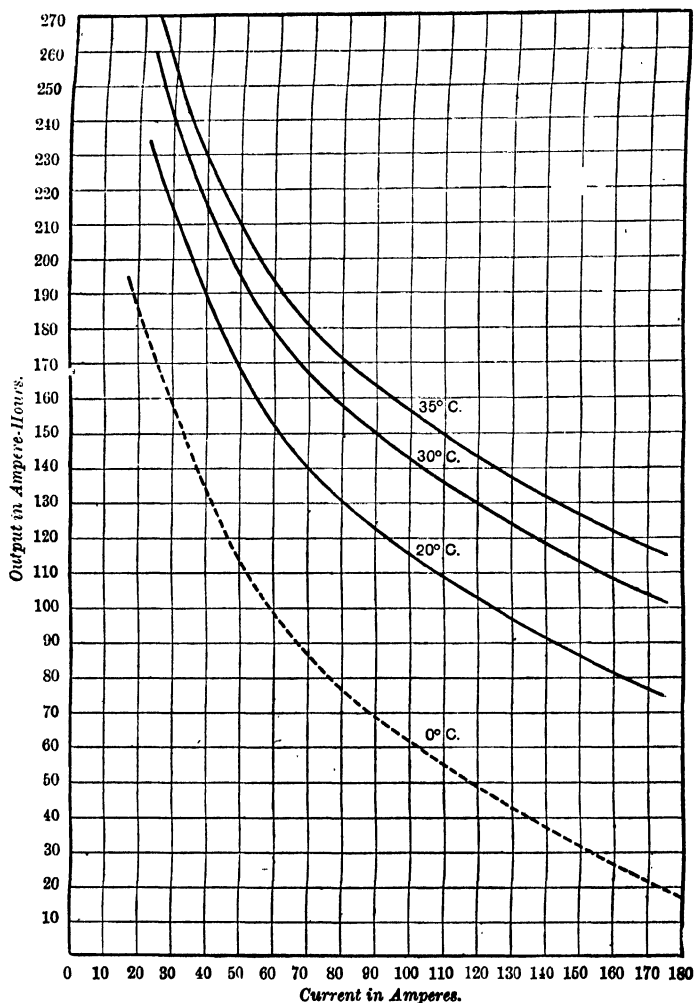


FIG. 152.—Variation of Output with Discharge rate at different Temperatures.

PROPERTIES OF LEAD CELLS

discharge rates. Only in the case of the discharge at 25 amperes does the curve of output begin to flatten at the higher temperatures, showing that here the maximum output of the active materials is being approached and cannot be much further augmented by merely improving the diffusion and diminishing the liquid polarisation.

The actual rise of output observed varied between 2.55 and 2.8 ampere-hours per degree Centigrade, the average being 2.7 ampere-hours per degree Centigrade, but this figure would no doubt vary somewhat for every different make of cell according to the type of the electrodes, their disposition relatively to each other, and other details.

The dotted portion of the curves in Fig. 151 are simply their prolongations down to 0°C. on the assumption that they still remain straight lines. The curves in Fig. 152 are constructed from the data furnished by the curves in Fig. 151, and show the variations of output with discharge rate for a few different temperatures.

Efficiency.

The electrical efficiency of a cell is the ratio of the ampere-hours or watt-hours given out on discharge to those required to effect its recharge *and restore it to precisely the same condition as at first*. Without this last proviso, efficiency figures have little meaning, and are comparatively valueless. The difficulty is to decide from what point to reckon. Emptiness (*i.e.*, complete sulphation and exhaustion of E.M.F.) cannot be adopted, because, as we have seen, a cell is never really emptied; and any attempt to do so involves injury to the electrodes and conditions of working which are never followed in practice. Fullness (*i.e.*, thorough desulphation) is a more realisable state, but, if cessation of the rise of P.D. on recharge is accepted as its criterion, only by the expenditure of a considerable amount of energy, for which no useful return can be obtained; and, on this account, cells are not often quite filled, especially when efficiency tests are going to be made. It is, so to speak, impossible to fill a cell just to the brim and no more; to get it full some must be allowed to run over, and to make sure of its being quite full a good deal must be lost in this way.

The only remaining alternative is to discharge and recharge the cell between two arbitrary limits, which, to ensure the efficiency covering its whole working range under practical conditions of usage, are preferably its ordinary end P.D.s of discharge and recharge, corresponding respectively to nominal emptiness and approximate fullness; and either one of these limits may be regarded as the starting point of the cycle. Seeing, however, the number and variety of the causes which affect and modify the P.D., a return to any given value does not by itself necessarily indicate that the cell is in the same state as when last there. Indeed, Ayrton showed that the opposite is usually the case, for, working in this way, he obtained a number of impossible figures, such as ampere-hour efficiencies from 100 to over 111 per cent., and even watt-hour efficiencies of more than 100 per cent.; while they varied amongst themselves according as the rates of discharge and recharge were altered. To make the method fulfil the essential requirement, the cells had to be put through a number of cycles of treatment identically the same time after time, and then at length the results became uniform and reasonable.

An efficiency so determined is scientifically correct, but its value, though definite, is limited, as it only holds good for the precise set of conditions under which it was obtained. For commercial purposes the average efficiency of a number of cycles of varying treatment spread over a considerable period, such as would be experienced in ordinary working, is generally far more useful. The difficulty of ensuring that the cell shall be in just the same state at the beginning and end of the test is not then felt, for any error in this respect is distributed amongst a good many discharges and becomes insignificant.

The ampere-hour efficiency of a cell will, of course, be diminished by external leakage or internal shunt circuits between the electrodes; and local action from whatever cause between either of the active materials and the electrolyte will have the same result. It used at one time to be supposed that some of the surplus charging current was expended in oxidising the metallic portion of the positive electrodes, but in reality the amount of such action that normally goes on during a single cycle of discharge and recharge is exceedingly

small, and it cannot be otherwise unless the cell is radically defective. These causes apart, ampere-hour efficiency really depends upon the degree of completeness to which the recharge is carried, the whole of the wasted current being represented by the generation of an equivalent quantity of hydrogen at the negatives and of oxygen or superoxidised products at the positives. By stopping the recharge at an early stage when hardly any gas has been evolved, almost perfect ampere-hour efficiency may be realised, but the desulphation of the active materials will then be very incomplete, and, besides the immediate output of the cell being proportionately reduced, a continuance of such treatment would permanently lower its capacity and seriously impair the life of the electrodes. Ayrton obtained ampere-hour efficiencies from 95 to over 98 per cent. with a 2.4 volt limit, and although this was not abnormally low when the slow rate of charge is considered, yet the P.D. was still rising rapidly at that point, and it is doubtful whether it was high enough for the maintenance of the cells in thoroughly good condition if their treatment had been severe in other respects. Allowing for rather more prolonged charging, ampere-hour efficiencies ranging between 90 and 95 per cent. are probably as much as can be expected in practice.

Losses of energy due to internal resistance, liquid polarisation by concentration or dilution of the acid round the electrodes, and gaseous polarisation on recharge, do not show themselves in the ampere-hour but only in the watt-hour efficiency, because their effect is confined to lowering the P.D. of discharge and raising that of recharge. It is here that efficiency comes most directly under the control of the manufacturer, for the amount of the difference between the mean P.D.s of discharge and recharge is largely dependent upon the design and construction of the cell. Under the most favourable conditions, however, the one always exceeds the other by at least 0.2 volt (say 2.15 and 1.95 volts respectively, with electrolyte of the usual strength), and so a watt-hour efficiency of about 90 per cent. is the most that could be realised even if the ampere-hour efficiency were practically perfect. As this is not the case, and as the difference between the discharge and recharge P.D.s is

generally somewhat greater than that just quoted, watt-hour efficiencies are seldom as high as 85 per cent. In Ayrton's experiments 87·4 per cent. was the maximum figure, but the circumstances were then exceptionally favourable to the very best results, because not only did the discharges and recharges follow continuously one upon the other, but they were effected very slowly—about a 12-hour rate in most cases. The shorter the interval on open circuit between a discharge and a recharge, or *vice versa*, the less will be the losses due to local action of all kinds or to inequalities of acid strength at the electrodes. High discharge and recharge rates not only reduce efficiency by increasing the expenditure of energy—which, of course, goes up as the *square* of the current—in overcoming the true internal resistance of the cell, but on recharge they also augment the polarisation, which behaves much like an additional internal resistance and causes a further waste in heat effects. For these reasons, charging at constant potential, however much it may improve the output of a cell, can never be so efficient as charging at constant current, and in the experiments of Cohen and Donaldson, already described, the former only yielded a watt-hour efficiency of 70·5 per cent. as against 81 per cent. by the more usual method. The difference in ampere-hour efficiency was only 2 per cent., the figures being 93·5 and 95·5 respectively, and this shows clearly where most of the extra loss was experienced.

Efficiency of Traction Batteries.

It has already been explained that, in order to obtain efficiencies under conditions which best correspond to those of ordinary usage, they are generally calculated in terms of the ratio between the ampere-hours or watt-hours of *complete* normal discharge and *complete* recharge. This method, however, does not in the least indicate what may be the efficiency of batteries receiving entirely different treatment, as is the case when they are introduced into traction systems to equalise the load on the generators—either simply “floating” on the line or combined with some kind of boosting device. The normal work of the cells then consists of innumerable cycles

of discharges for a few seconds or minutes at very high and variable rates, and recharges on the same scale, following one another without intermission. In a well-adjusted system the mean output and intake are equal and the battery is never discharged to anything approaching completeness; or, if so nice a balance cannot be maintained, this is prevented by an occasional continuous recharge.

Considering the high rates of discharge and recharge it would seem inevitable that traction regulator batteries must have a lower efficiency than if used in a more ordinary manner, but the general consensus of opinion amongst those in a position to judge is that, on the contrary, it is distinctly higher. For instance, J. S. Highfield* found that the watt-hour efficiency during a twelvemonth's working of a central station lighting battery was 74 per cent. under favourable conditions as regards regulation and treatment; whereas a traction battery yielded 84 per cent. efficiency, which figure is not far short of the maximum that can be realised in the most careful laboratory tests on the usual lines.

The causes of this apparent anomaly have been disclosed in a very interesting investigation made by B. Hopkinson† into the losses of energy in accumulators when working under approximate traction conditions. His experiments were made upon two Tudor and one Chloride cell, each having an output of 7 amperes for nearly one hour (*see* Fig. 153.) The method adopted was to discharge one or other of the cells at constant current for some short period of time, ranging from 10 seconds to 15 minutes, then reverse the current and recharge at the same rate for the same time. This constituted a "cycle," and when it had been continuously repeated for a sufficient number of times, uniform P.D. readings, from which curves could be plotted and efficiencies calculated, were obtained. Before each set of tests the fully charged cells were about one-fourth discharged at a moderate current so that no evolution of gas should take place during the recharges in the experiments proper. Owing to this precaution it could, under the special circumstances, be assumed that the ampere-hour efficiency of the cell was perfect; and the watt-hour efficiency

* *Journal I.E.E.*, Vol. XXX., p. 1,070.

† *The Electrician*, Vol. XLVIII., p. 211 (November 29, 1901).

was directly computed in terms of the ratio of the mean P.D. of discharge to that of recharge. Fig. 154 shows the P.D. curves of one of the Tudor cells when put through one-minute, ten-minute and thirty-minute cycles—A, B and C respectively—all at a current of 2.7 amperes. The three upper curves of recharge P.D. are plotted from left to right in the usual way but the three lower curves of discharge run from right to left so as to conform to the cyclic character of the operation. The area enclosed between each pair of curves is proportional to the energy dissipated, and as each is plotted

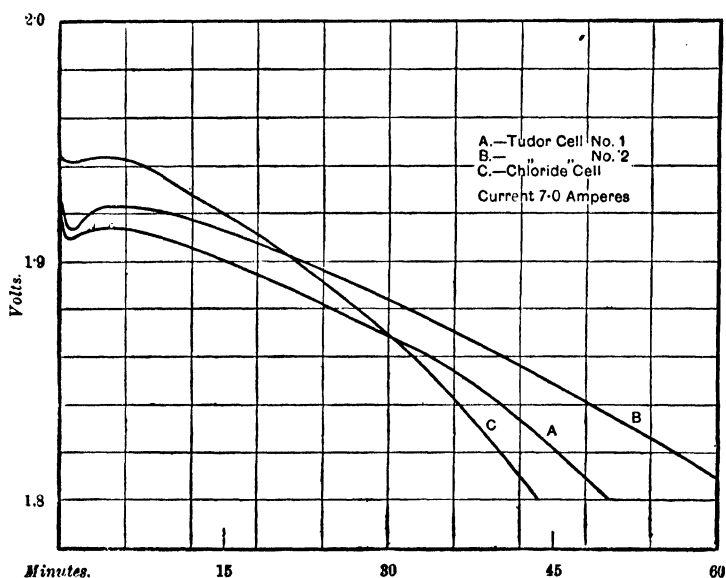


FIG. 153.—Hopkinson's Efficiency Tests. Curves of Discharge P.D. of Cells Tested.

according to different scales of time which are in inverse ratio to the length of the cycle, the areas may be directly compared as regards the energy dissipated in the same total length of time or the passage, in and out, of the same amount of current. That is to say, area A accounts for 30 one-minute cycles; area B for 3 ten-minute cycles; and area C for 1 thirty-minute cycle. Fig 155 gives curves scaled in the same way for the Chloride cell working through ten-minute, one-minute, and twenty-second cycles.

The contention of the writer of the Paper that the efficiency of the cells increases as the time of the cycle decreases, is clearly established by his curves, of which several other sets are given, besides those reproduced here. He concludes that for cycles having very short periods between 1 second and 10 seconds, the percentage dissipation of energy is practically constant and may almost all be accounted for by the internal

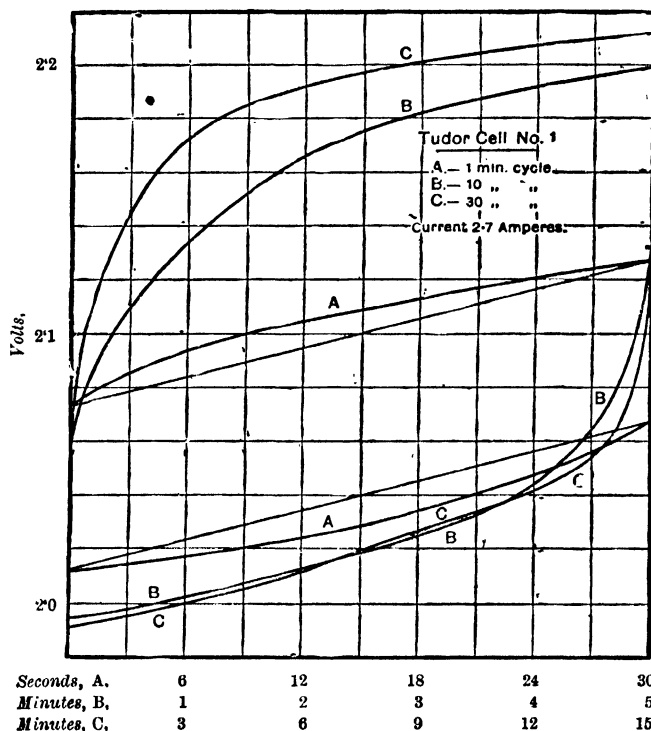


FIG. 154.—Hopkinson's Efficiency Tests. Short Cycles of Discharge and Recharge P.D.

resistance ; although, be it noted, this resistance, as measured, is far larger than the calculated resistance of the layers of electrolyte between the plates. As the cycle lengthens, an additional loss of energy, over and above that due to resistance, gradually assumes larger proportions and accounts for the reduction of efficiency. This he terms "electrolytic

dissipation," and it is evidently identical with what is more generally called polarisation.

The actual efficiency figures are remarkably high. For discharges at less than a one-hour rate (7 to 8 amperes), and one-minute cycles—conditions very similar to those of a traction battery in full work—the energy efficiency is between 90 and 91 per cent., while for twenty-second cycles it rises to

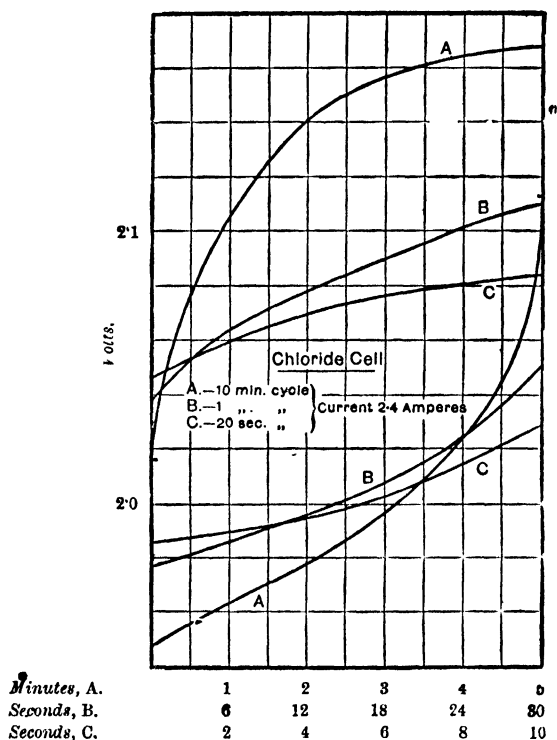


FIG. 155.—Hopkinson's Efficiency Tests. Short Cycles of Discharge and Recharge P.D.

nearly 92 per cent. Ten-minute cycles, at the same rate, give about 87 per cent. efficiency, which, although high, means a loss of about 35 per cent. more energy than in one-minute cycles. With a discharge rate of 2.4 or 2.7 amperes—corresponding to a lightly worked traction battery—the efficiency rises to nearly 97 per cent. for one-minute cycles, and 93.5 per

cent. for ten-minute cycles, these being the cases dealt with in Figs. 154 and 155. It is evident therefore that an increase of current rate does pull down the efficiency, whether the cycle be of the shortest or whether it includes the entire discharge and recharge of the cell, but that in the former case the saving effected by the elimination of polarisation more than outweighs the loss, and thus explains why the ultimate efficiency is higher.

It cannot be expected that, in practice, traction batteries will work for long periods together quite so efficiently as the foregoing figures would indicate, for at times when the cells are already nearly fully charged and still receiving current at very high rates considerable quantities of gas will be evolved and the preliminary assumption of 100 per cent. ampere-hour efficiency is at once upset; and in any case the cells will occasionally require to be charged beyond the gassing point, for the sake of keeping them in good condition.

With regard to the precise direction in which the saving of energy on short cycles is effected, it seems pretty evident from the curves that it is the reduction of gaseous polarisation on recharge which makes all the difference. This is very apparent in Figs. 154 and 155. Whatever the length of the cycle, the curves of discharge P.D. keep fairly close together, although there is of course some difference caused by more or less liquid polarisation, but on the recharge the curves for ten-minute and thirty-minute cycles rise rapidly above those of shorter period.

Internal Resistance.

By reading the E.M.F. of a charged storage cell with a dead-beat voltmeter, first when discharging at a known rate, and again directly the circuit is broken, fairly accurate determinations of its internal resistance may be made. The figures obtained show that, relatively to its output and the rate at which it can be satisfactorily discharged, a lead/sulphuric acid/lead peroxide cell has a lower internal resistance than any other practical type of galvanic element. This is owing to the very low specific resistance—as solutions go—of its dilute acid electrolyte, the close proximity of its electrodes, and its small amount of polarisation. The actual internal

resistance of any cell largely depends of course upon the area of the opposed surface afforded by the electrodes and the distance between them. Ayrton specially investigated the latter point and proved its correctness, for, although it could hardly be otherwise, it did not appear to be in accord with other measurements that had been made.

In 1885 Preece* called attention to the fact that the internal resistance of an accumulator depended to some extent upon the amount of current passing at the time of measurement, the stronger the current the less being the resistance. The same observation has since been confirmed by Streintz and others. It was thought at one time that this property would prove of some importance in the commercial applications of lead cells, by enabling them to automatically maintain a constant terminal P.D., irrespective of the rate at which they were discharging, and so behave like a compound-wound dynamo. Such has not, however, been the case, possibly because the effect is too small or is counteracted by a decrease of the effective E.M.F. with increased current; but, apart from this, it has never yet been clearly shown whether the resistance itself does remain permanently less at higher discharge rates or whether it is only a temporary reduction. The latter result might be anticipated from a consideration of the increased surface of active material at first brought into play, but it hardly seems likely that this state of affairs should persist for any considerable length of time.

In most cells the layers of acid between the electrodes do not play much part in the alterations of internal resistance that occur during discharge, because their variations of strength only correspond to comparatively small differences of specific resistance; and the main seat of these changes is in the active materials and the electrolyte immediately surrounding them. The nature of the changes has already been indicated from *a priori* considerations, but it is not easy to confirm them by direct measurements of internal resistance on account of the difficulty, due to polarisation, of measuring the E.M.F. that is really acting on closed circuit. The longer the discharge is continued the more pronounced do these difficulties become, and consequently our knowledge and records of internal

* *The Electrician*, Vol. XV., p. 42, May 29, 1885.

resistance from actual observation are almost entirely confined to charged cells or the earlier stages of their discharge. The curve of internal resistance in Fig. 130, page 151, which is based upon values for the effective E.M.F.s, obtained by a method already described, shows some inconsiderable rises and falls during the first half of the discharge. No doubt these would present some differences of position and degree in every different cell, but taken as a whole the curve confirms the generally accepted view that in most cases the internal resistance of a lead cell remains fairly constant throughout the major portion of the discharge and then increases rapidly towards the end.

At that most interesting point in the discharge of a cell where the sudden break occurs in the P.D. curve, the polarisation has attained its maximum value and its effects upon the E.M.F. are so intermingled with those due to the internal resistance that there is great difficulty in discriminating between them. This is partly why the enormous increase in the internal resistance of the cell at this stage, due, as the author believes, to a corresponding increase in the specific resistance of the active materials, is not readily recognised. If there were no liquid polarisation, the E.M.F. of the cell would recover its full open-circuit value the instant the discharge was stopped, and its high resistance could not then be overlooked. Instead, what generally happens is that the instantaneous rise of E.M.F. is only partial, and merges into a further rise which takes more or less time for its completion, thus giving the superficial impression that the whole effect is one of a gradual recovery of E.M.F.

The most striking indication however, as to the order of the internal resistance of an exhausted cell is sometimes obtained when attempting to measure its open-circuit E.M.F. with a high-resistance voltmeter. On closing the voltmeter circuit the first reading may be nearly 2 volts, but a rapid decrease immediately sets in and in the course of a few minutes, or even seconds, the needle travels steadily back to zero, thus showing that the extremely small current passing is sufficient to force up the internal resistance until that of the instrument, amounting perhaps to some hundreds of ohms, becomes relatively negligible. The writer has repeatedly

observed this effect, but it was noted by Griscom* in 1894, and he also gave curves showing the enormous increase of internal resistance. It is now evident why thoroughly discharged cells do not apparently always recover their full E.M.F. even after a prolonged rest on open circuit, the fact being that the E.M.F. is there but that under the circumstances an ordinary voltmeter is incapable of indicating it, and results of any value are only to be obtained from some "null" method which does not require the passage of a current. These remarks do not, of course, apply to cells which are merely "discharged" in the sense that their P.D. has been pulled down below some arbitrary limit by local weakening of the electrolyte, and are still capable of giving further output at a lower P.D. or current rate or after a rest on open circuit, but only to such as have practically reached the limit of their discharge under any conditions.

Fig. 137 gives the curve of internal resistance on recharge for the same cell whose discharge resistance was shown in Fig. 130. Here, again, there are small variations of resistance during the earlier portion of the recharge, due most probably to the local changes and inequalities of the strength of the electrolyte round the electrodes; and, again, a rapid rise of resistance towards the end. This rise sets in at just about the same time that the upward turn of the curve of effective E.M.F. commences, and there can be little doubt that they are both due to the same cause—namely, the increasing gaseous polarisation consequent upon the active materials being no longer able to absorb the whole of the current. It must be remembered that this high resistance is not a permanent attribute of a charged cell like an ordinary internal resistance, for it varies in amount with the strength of the charging current, and on open circuit it diminishes and passes away more rapidly than the high E.M.F. which accompanies it. On comparing the curves in Figs. 130 and 137 it may be noticed that although the discharge followed immediately upon the recharge, the resistance at the commencement of the discharge is quite low and normal, and gives no indication whatever of the high value it had attained when the recharge ended.

* *Trans. American Inst. Elec. Eng.*, Vol. XI., p. 302, May 16, 1894.

It is, indeed, open to question whether it is internal resistance at all in the usually accepted sense of the term. Much ingenuity has been spent in devising methods which will really measure effective closed-circuit E.M.F.s, and so enable permanent internal resistance to be discriminated from transitory polarisation effects, but it is doubtful whether any of them, even those based on the use of condensers or time curves of fall of E.M.F. after breaking circuit, do entirely accomplish the desired object. In some cases, especially when the polarisation is of a gaseous nature, as in the present instance, resistance and counter E.M.F. merge so closely into each other as to suggest that they are perhaps only two different aspects of one and the same phenomenon.

CHAPTER V.

THE CHEMISTRY OF LEAD CELLS.

Historical.

Planté not only constructed the first practical lead accumulators, but he also very carefully studied the theory of their action, and his views were in some respects more correct than those held at a considerably later period. He clearly recognised that the high E.M.F. of the cell resulted from the combined effect of the deoxidisation of the lead peroxide and the oxidisation of the metallic lead, but he seems to have considered that the normal discharge reaction was for the peroxide to be reduced right down to the metallic state and for the lead to be oxidised nearly if not quite up to the stage of peroxide; whether the formation of peroxide at the negative electrode was actually observed by him is not very definitely stated, although he is generally assumed to have done so. He made no mention whatever of any combination between the sulphuric acid in the electrolyte and either of the active materials. Emile Reynier says that Planté was well aware of the production of lead sulphate, but did not believe it to be a normal result of electrolytic action, so probably he was only acquainted with the white irreducible form of sulphate which may sometimes have appeared in his cells when they had been left for a long time on open circuit.

During the period immediately following Faure's introduction of electrodes pasted with lead oxides, the occluded gas theory appears to have been almost exclusively adopted. In accordance with the views held at that time as to the nature of electrolysis, it was assumed that sulphuric acid merely

increased the conductivity of the water, which was the real electrolyte, and when a current passed through the cell became decomposed into its constituent gases, which were liberated and absorbed at their respective electrodes. It was known that the oxygen first peroxidised all the positive active material, but more gas was supposed to then be occluded. The well-known property of absorbing oxygen or hydrogen possessed by palladium, platinum, and, in lesser degree, by a few other metals, especially when in a spongy or finely-divided state; Grove's gas battery, and Siemens' experiments on gas batteries built up of carbon plates saturated with salts of lead were the chief facts on which the theory was based; and the large capacity of Faure type electrodes was put down to the enormous surface afforded by their porous mass of reduced oxides.

In a series of articles on "Electric Accumulators or Secondary Batteries," which commenced in the *Engineer*, in May, 1882,* Dr. Oliver Lodge propounded what were no doubt the most advanced views hitherto accepted. The activity of the negative electrode was solely ascribed to occluded hydrogen, while the reduction of peroxide to monoxide was recognised as the essential reaction at the positive; and what was supposed to be the subsequent secondary combination of this monoxide with sulphuric acid also noted. A number of experiments on the formation of "scums" or films of white sulphate at the negative were described, but this, as well as its oxidation, was supposed only to occur when the hydrogen became exhausted, taking the form of a crust of non-conducting materials that first appeared at the surface in free contact with the electrolyte, and gradually increased in thickness as it spread inwards. In fact, the formation of sulphate under any circumstances was regarded as an unmitigated evil; so much so, that it was expressly stated that the presence of an excess of acid in the cell must be avoided, because it conduced to the too easy production of this compound at both electrodes.

Almost contemporaneously with Dr. Lodge's articles, some others by Dr. J. H. Gladstone and A. Tribe, dealing only with the chemistry of the cells, appeared in the columns of *Nature*,† and these, afterwards collected and published

* Reproduced in *The Electrician*, June 10, 1882, and *seq.*

† *Nature*, January 5, 1882, and *seq.*

in book form,* constituted the most important contribution to the subject that had so far been made, because for the first time they propounded a theory of the various reactions, based upon data obtained from actual analyses. They demonstrated that the spongy lead at the negative only absorbs the merest trace of hydrogen on charging, and that the normal discharge reaction is its direct combination with sulphuric acid (SO_4) to form lead sulphate. They further showed that at the positive lead peroxide is also converted into lead sulphate, so that the total result of the discharge was the formation at both electrodes of lead sulphate at the expense of the sulphuric acid in the electrolyte, which was replaced by an equivalent quantity of water. This new theory gave rise to considerable controversy at the time between Messrs. Gladstone and Tribe and Dr. Lodge. To the latter it seemed highly improbable that the correct explanation of the cell's action could be one which involved the production of large quantities of non-conducting insoluble lead sulphate, however strong the evidence by which it was supported. Lord Kelvin (then Sir William Thomson) and Dr. Lodge had both failed in their attempts to reduce white lead sulphate by electrolysis in dilute sulphuric acid, although it could be peroxidised with some difficulty; and even the best of Gladstone and Tribe's own experiments showed that this reduction only took place very slowly and incompletely, and with an excessive expenditure of current energy. How, then, was it possible for a result, which otherwise needed many days, to be obtained in a cell in a few hours with a complete absorption of the current until only a very small percentage of sulphate still remained unattacked? In putting the chemistry of the cell upon a sounder basis Gladstone and Tribe had certainly rendered its physics proportionately difficult to understand.

Early in 1883† Dr. E. Frankland also proved experimentally that neither oxygen nor hydrogen is occluded by the charged active materials, and that the production of lead sulphate at both electrodes is the real reaction of discharge. As a corollary, he pointed out that the changes in the specific gravity of the electrolyte might be utilised to indicate the degree to which a

* "The Chemistry of Secondary Batteries" (1883).

† *Proc. Roy. Soc.*, Vol. XXXV. (1883), page 67.

cell was discharged. From this time onwards the double sulphation theory rapidly gained ground, receiving further corroboration from Reynier*, Crova and Garbet†, Tschelltzow‡, and many others.

Another important matter investigated by Gladstone and Tribe was the nature of the local action which occurs at the positive electrodes. Planté had observed that the lead peroxide speedily underwent reduction on open circuit, especially during the earlier stages of the formation of his electrodes, and he realised that this must be in some way due to the galvanic couple which it formed with metallic lead underneath, but he thought that the precise action consisted in the decomposition of water, and that this also accounted for the oxygen gas which was evolved for a short time after the cessation of charging. Gladstone and Tribe came to the conclusion that what actually happened was a reduction of the peroxide to sulphate, accompanied by the formation of an equal quantity of sulphate out of the lead surface in contact with it—another case, in fact, of double sulphation, but with the positive lead support taking the place of the spongy lead active material of the negative electrode. A valuable outcome of the acceptance of the double sulphation theory of discharge was a recognition of the necessity for supplying cells with stronger acid and more of it, so that normal sulphation could easily take place without the electrolyte becoming too weak; but its application to explain local action at the positive gave rise to very exaggerated ideas as to the rate at which the metallic supports could be oxidised, and to false views regarding the treatment necessary to prevent their destruction. Users of cells were warned never to fully charge them, as it was supposed that a skin of sulphate which protected the plates would then be peroxidised and their corrosion very much accelerated.

In 1886,§ however, B. M. Drake and J. M. Gorham showed that the real protective coating was the adjacent peroxide itself, and that overcharging was decidedly beneficial, as it maintained this in good condition and attacked any residue of

* Société Française de Physique, April 4, 1884.

† *Comptes Rendus*, January 1, 1885.

‡ *Comptes Rendus*, June 8, 1885.

§ British Association, 1886. *The Electrician*, September 19, 1886.

sulphate that was present elsewhere. On the other hand, they found that the over-discharging then generally practised was the real cause of the excessive sulphating, buckling and local action to which the electrodes were so liable. From a practical point of view their conclusions were of the greatest value, for they entirely revolutionised the methods of treatment formerly adopted, and introduced others which still form the basis of all successful working.

Since the early eighties the definite additions to the theory and chemistry of lead cells have been very few; and this not because little yet remained to be explained, but because the frequent suggestions and hypotheses which endeavoured to clear up the many outstanding difficulties could seldom be established with certainty. The excess of white sulphate formed under some conditions seemed to point to the existence of two different kinds of sulphate, one reducible and one not, and various theories of double and basic salts were put forward. In 1889* Frankland made some experiments which appeared to indicate that two basic sulphates, $3\text{PbSO}_4 \cdot 2\text{PbO}$ and $\text{PbSO}_4 \cdot \text{PbO}_2$, were obtainable by the action of dilute sulphuric acid of litharge and minium respectively, and those, he thought, might be reproduced in the cell on discharge; but Gladstone and Hibbert,† and also Robertson,‡ consider they are only mixtures of normal lead sulphate with more or less oxide. The Paper by Ayrton on "The Chemistry of Secondary Cells," read before the Institution of Electrical Engineers in 1890,§ did not propound any new theory of their action, but it supplied some very valuable data obtained from commercial cells working under practical conditions, as to the composition, both qualitative and quantitative, of their active materials at various stages of charge and discharge. Their investigations also included an examination of the temperature changes of a working cell, and these, together with some experiments made by L. Duncan and H. Wiegand and communicated to the American Institute of Electrical Engineers

* *Proc. Roy. Soc.*, Vol. XLVI., p. 304.

† *Proc. Phys. Soc.*, 1890, Vol. X., p. 448, and Vol. XI. p. 44.

‡ *Proc. Roy. Soc.*, 1891, Vol. L., p. 105

§ *Journal I.E.E.*, Vol. XIX., p. 660

in 1889,* form the first definite contributions to this branch of the subject.

Most researches of later years have centred round the need for some fuller and more satisfactory explanation of the various changes in the E.M.F. and P.D. of lead cells, and this has necessitated a much closer consideration being given to the exact constitution of the electrolyte. As long ago as 1883, J. Swinburne suggested that the weakening or strengthening of the acid solution in the pores of the active materials would have some effect on the E.M.F. In 1889 Duncan and Wiegand, in their communication just referred to, showed that during discharge its strength was most probably very greatly reduced by the abstraction of acid to form sulphate far faster than it could be restored by diffusion from outside; and following the same line of argument Gladstone and Hibbert endeavoured to prove that the E.M.F.s observed under every condition of usage could all be accounted for in terms of variations of acid strength. Their first results were made public in 1890,† but they go most fully into the matter in an interesting Paper "On the Cause of the Changes of Electromotive Force in Secondary Batteries," read before the Institution of Electrical Engineers in 1892.‡ In it they deal with the high E.M.F. observed immediately on the cessation of charging, the normal variations of E.M.F. during discharge and recharge, and the loss of E.M.F. with over-discharging or heavy discharge rates and its subsequent recovery on open circuit.

Their conclusions in their entirety met with considerable opposition and criticism, and in some quarters it was considered that the presence of peroxides in the electrolyte was a far more potent factor than mere changes of acid strength. Planté had noted the formation on charging of some unstable compound containing an excess of oxygen—presumably hydrogen peroxide—and had ascribed the high initial E.M.F. of a freshly-charged cell to its presence; and he was also aware that persulphuric acid, the highly oxidised compound discovered by Berthelot in 1878, was a direct product of the electrolysis of

* *Electrical World*, Vol. XIII., p. 347, June 15, 1889.

† *Proc. Phys. Soc.*, Vol. X., p. 448.

‡ *Journal I.E.E.*, Vol. XXI., p. 12.

dilute sulphuric acid. In 1883* Gladstone and Tribe detected persulphuric acid in some solution that had been subjected to electrolysis, and in 1891† Dr. H. E. Armstrong and G. H. Robertson called attention to the probability that this substance was the real cause of many obscure phenomena observed in lead cells. The latter gentleman propounded this view in more detail in a Paper read before the Society of Arts in the same year.‡ He maintained that persulphuric acid and hydrogen peroxide were always formed in considerable quantities at the positive electrodes during recharging, their relative proportions depending on the acid strength and other conditions; and he considered that a cell's E.M.F. was in some way related to the presence of these compounds.

From the time of the first enunciation of the double sulphation theory of discharge down to the present day there have always been some who dispute its accuracy, except in a more or less modified form. Apart from other objections, it appeared to them that to assume a powerful E.M.F. could result from the production of one and the same substance—normal lead sulphate—at *both* electrodes was to violate the fundamental principles of electrolysis. Whilst, therefore, generally acknowledging the direct sulphation of the negative active material, they maintain that the reduction of lead peroxide to a lower stage of oxidation is the only true electrolytic action at the positive. They admit that lead sulphate is also formed there, but consider this to be an after effect which does not contribute anything to the cell's E.M.F.; and, further, they deny that the amount of sulphate bears any definite relation to the ampere-hours yielded by the cell, but merely depends upon the strength of the acid, the length of time for which the reduced active material has been exposed to its action, and other secondary causes. This view always found one of its chief supporters in Desmond FitzGerald, who first stated his case in letters appearing in *The Electrician* in 1885, and since then has reaffirmed it on many occasions.§ He believes that the peroxide is not reduced to monoxide on discharge, but only to

* *Journal Chemical Society*, 1883, p. 345.

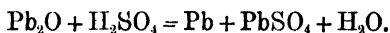
† *Proc. Roy. Soc.*, Vol. L., p. 105.

‡ *Journal Society of Arts*, Vol. XL., p. 44.

§ *Journal I.E.E.*, Vol. XVI., p. 168, March 10, 1887.

sesquioxide (Pb_2O_3), a compound very akin in its nature to red lead.

In 1892 a new champion for the oxidation theory came forward in the person of M. G. Darrieus, who, in a Paper read before the Société Internationale des Electriciens, advanced quite a number of original views. According to his experiments, not only was the conversion of the positive active material into lead sulphate purely incidental and partial, but he also argued that the sulphation of the negative material occurred in two stages—first, an oxidation to sub-oxide (Pb_2O), and then a local action with the acid to form lead sulphate and metallic lead:—



In this instance, however, the decomposition of the oxide was assumed to follow immediately on its production, and the formation of sulphate to be directly proportional to the current passing. He appeared to think that at the positive the peroxide is reduced right down to monoxide before sulphation, and that the discharged active material is chiefly a mixture of these two oxides. He further maintained that the electrolytically-prepared spongy lead at the negative electrode is in a special molecular or allotropic condition which enables it to furnish considerably more E.M.F. and energy by its sulphation than lead can do in its ordinary solid form. FitzGerald had long before pointed out that electrolytic peroxide differed somewhat in its properties from that which was chemically prepared; and in 1900* the Author endeavoured to furnish an explanation of some of the outstanding difficulties connected with the discharge reactions, starting from the assumption that *both* active materials were in an allotropic state and possessed of a highly complex molecular structure. These views are given in detail further on in this chapter.

The foregoing brief historical account of the development of the chemical theory of the lead accumulator does not profess to include everything that has been written on the subject, especially abroad, but it is believed that all the principal lines of thought are represented. The position at the present day may be summed up in a few sentences. Although the double

* *Journal I.E.E.*, Vol. XXIX., p. 460, March 22, 1900.

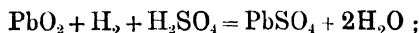
sulphation theory put forward twenty years ago by Gladstone and Tribe still receives general acceptance, yet it has from the first been felt that in its original form it left many things unexplained, and rendered some of them very difficult of explanation; and the intervening period has seen many attempts, to which the authors of the theory have contributed their share, to supply the deficiency. While a few have been based on a total dissent from the main proposition of double sulphation, the majority have only sought to amplify or modify it, but whether, or how far, any one of them is entitled to rank as established fact remains largely a matter of individual taste or judgment.

The success with which, during the last few years, the dissociation hypothesis has been applied to the elucidation of many diverse and obscure chemical phenomena, at first sight suggests that it might have some authoritative word to say on the settlement of the questions now at issue. A number of writers, mostly in Germany, have discussed the matter from this point of view, but a perusal of their work makes it abundantly clear that, whilst differing greatly amongst themselves, they are all alike in their entire failure to throw any light on whatever is at present unknown or uncertain, and can only with difficulty frame a nominal explanation in terms of the theory of electrolytic dissociation of the reactions thought to take place. Not, of course, that the theory is defective, but that its scope is not as yet wide enough to embrace substances like the active materials of lead cells, which are neither electrolytes nor capable of passing between the molecular and ionic states, but remain practically insoluble under all conditions of usage. On this account it seems best for the present to make but a sparing use of the conception of dissociation, as it invariably involves one in a number of minor assumptions which eventually may prove more or less incorrect and only add to the difficulties already surrounding the subject.

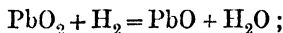
The Oxidisation Theory of Discharge.

No one now disputes that sulphuric acid is the real electrolyte, water acting as the solvent, and it is usually assumed that the acid is dissociated into H and SO_4 ions; but should it be broken up in some other way, such as H and HSO_4 , or

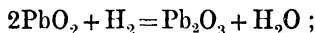
should some hydrated acid, such as $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} = \text{H}_6\text{SO}_6$, be dissociated, it would not materially affect the points about to be considered. It is also generally admitted that, on closing the external circuit, SO_4 combines with the spongy lead of the negative electrode to form a lead sulphate—the precise nature of this compound will be more fully considered presently—the amount passing into combination being directly proportional to the quantity of electricity generated. At the positive electrode, hydrogen ions react with the lead peroxide, reducing it with the production of water. And, again, it is agreed that the quantity of oxygen abstracted from the peroxide is also proportional to the total current output. But here arises the divergence of views. Does the positive active material, as Gladstone and Tribe asserted, combine with as much SO_4 as the negative active material



is it merely reduced to monoxide, as Darrius maintains,



or, as FitzGerald believes, only to sesquioxide ;

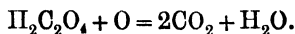


and is any sulphation that occurs a quite unessential and incidental reaction? The answer to these questions may be sought by examining the direct experimental and analytical evidence; the chemical characteristics of the various compounds involved; and the relationship of the reactions to electrochemical theory and the E.M.F. of the cell. If the first of these three methods yielded absolutely conclusive results, there would be little need to consider the other two, but, unfortunately, this is hardly the case. For various reasons, the difficulty of obtaining complete and accurate analyses of the active materials during the working of a cell are so great that very few thorough investigations of the kind have been made, and not one perhaps that is entirely free from all possible sources of error. The bulk of the evidence, however, from Gladstone and Tribe onwards, and especially that published by Ayrton in 1890, is clearly in favour of double sulphation, and the minority, which seemed to indicate that the sulphation at the positive is uncertain and incomplete, has mostly been of

a very fragmentary nature; indeed, Darrieus' results excepted, hardly merits serious consideration.

The old idea, in which the Author shared, was that the lower oxides of lead cannot exist as such in the presence of free sulphuric acid, but are rapidly converted into normal lead sulphate or broken up into mixtures of sulphate and peroxide. The experiments of Frankland and of Gladstone and Tribe on basic lead sulphates showed that powdered litharge offers a very considerable resistance to complete sulphation by dilute acid, and FitzGerald, who has observed the same fact, considers that it furnishes an argument against sulphation at the positive electrode; but, until it is proved that litharge is ever produced there, the conclusion is hardly justified. Quite apart from this, however, it seems extremely likely that the sluggishness of the lead oxides in reacting with an acid with which they form an insoluble salt is partially or wholly accounted for by what may be termed a mechanical rather than a chemical reason. A lump of solid litharge—obtained by fusing and then cooling rapidly—would obviously not be more than superficially attached in a solution of sulphuric acid, and it is quite possible that the same cause may operate in a lesser degree in the case of the powder—*i.e.*, the liquid may not penetrate to the centre of the grains at all, or, even if it does so at first, the expansion of the anhydrous oxide, as it sulphates and hydrates, may entirely close up its pores and prevent enough acid entering to complete the reaction. Experiments with litharge fully confirm this view, for if it is prepared by a process which renders it thoroughly porous it can be entirely converted into white sulphate in the course of a few minutes without using more acid than is required for the combination.

But, instead of experimenting with lead monoxide for the purpose of throwing light on what happens to lead peroxide when discharging, a more direct and pertinent test may be made by supplying to lead peroxide, in the presence of free sulphuric acid, some agent which will play the part of the electrolytic hydrogen and abstract oxygen from it by chemical means. Oxalic acid serves this purpose admirably, for it acts as a powerful reducing agent, and on combining with oxygen is entirely resolved into carbon dioxide and water,



If finely powdered lead peroxide is placed in a considerable quantity of water, and a solution containing equivalent amounts of sulphuric and oxalic acids is then added in small quantities at a time, the liquid will (provided the relative proportions between the acids are correct) very soon give a neutral reaction with a suitable indicator, thus showing that the whole of the sulphuric acid has combined with the reduced oxide. The peroxide should be stirred after each addition to bring it in contact with the whole of the solution and facilitate the escape of the gas, and if litmus is used to test for acidity, the effect of the CO_2 must be allowed for. Naturally, the reaction is not completed quite as quickly as if a liquid such as a solution of caustic alkali were being neutralised, but its end is sufficiently well marked to prove that the reduced oxide has not the slightest tendency to remain unsulphated, even in the presence of the very weakest acid; and this behaviour continues until about two-thirds of an equivalent of sulphuric acid (and also of oxalic acid) has been added for each equivalent of peroxide used. Beyond that stage the liquid only loses its acidity very slowly, not because the sulphuric acid ceases to combine with the reduced peroxide, but because the reaction of the peroxide with the oxalic acid then becomes more and more sluggish and incomplete; and it appears to be impossible to entirely reduce it, even in the presence of a considerable excess of acid. That this is so may be proved by using oxalic acid alone, when it will no longer be decomposed after two-thirds of the peroxide has been attacked. The actual amount of acid needed will be twice what was required in conjunction with sulphuric acid, as half the oxalic acid now combines with the reduced peroxide to form an insoluble oxalate.

The original experiment may be varied by first adding all the sulphuric acid to the peroxide, and the oxalic acid afterwards; but the result will be just as conclusive up to the limiting value of a two-third equivalent of acid. The significance of this latter condition is considered later on, but, whatever its meaning, it does not affect the inference that the sulphation of the positive active material is a normal and inevitable discharge reaction, for it is almost certain that never more than two-thirds of the peroxide are reduced even at the end of the

most complete discharge, and generally the proportion attacked is not nearly so much.

The true reason why opposition to the double sulphation theory, although limited, is so persistent is not that the experimental evidence in its favour is insufficient or that it is chemically unsound, but because some people are unable to fit it in with their conceptions as to the nature of electrolysis. The objection that an E.M.F. cannot be obtained by the formation of the same compound at both electrodes is in itself of no account, for in the one case the sulphate results from the oxidisation of an electro-positive, and in the other from the reduction of an electro-negative substance, and the electrical effect of the two reactions is, therefore, additive; what difficulty there is lies more in the way in which the sulphate is produced at the positive electrode. Although there may be a direct conversion of lead peroxide into lead sulphate, it is almost impossible (unless the sulphuric acid is previously combined with the peroxide) to form any mental picture of what takes place without assuming that the hydrogen first reduces the peroxide, and that the lower oxide then becomes sulphated by what is termed a secondary action; but even should this be so, it affords no grounds for treating the sulphation as a casual heat-producing change only, without one is prepared to argue that all secondary actions are similarly non-electrolytic. The fact that a change of valency is involved, that the compounds are almost insoluble, and that it is not definitely known how they ionise, all tends to obscure the matter, and a full explanation in accordance with the dissociation or any other hypothesis is certainly not yet forthcoming; but, in principle, the reaction is in no wise different from those taking place when, say, a solution of potassium sulphate is electrolysed, and the potassium and the sulphion ions both react with water at their respective electrodes and form potassic hydrate and sulphuric acid.

It is helpful to remember that the lead peroxide in a cell is almost certainly hydrated and plays the part of a feeble acid. The reaction at the positive on discharge then becomes exactly analogous to that taking place in a "bichromate" cell. In the one case a mixture of plumbic and sulphuric acids is reduced to lead sulphate and water; in the other a mixture of

chromic and sulphuric acids is reduced to chromic sulphate and water; and, strangely enough, no one ever suggests that the chromic acid is merely reduced to chromic sesquioxide, which then combines with the sulphuric acid as an after-thought.

It is evident that the sulphation at the positive—and no one denies that a considerable quantity of sulphate is formed there during a discharge—must be either heat-producing or electrolytic. In the latter case the reaction will contribute nearly half a volt to the cell's E.M.F.; in the former, the heat generated will be quite sufficient to cause a considerable rise in its temperature. The result of Duncan and Wiegand's and of Ayrton's researches clearly proves, however, that, at most, a cell generates hardly any more heat on discharge than can be accounted for by its C^2R losses, perhaps not so much, or it may even absorb heat and fall in temperature; and having regard to this fact, it seems difficult to suppose that a strong local action is going on all the time. On the other hand, the E.M.F. of about 2 volts furnished at the commencement of a discharge is in full agreement with the E.M.F. calculated from the thermo-chemical data, if the double sulphation is included, but cannot be accounted for without it. This conclusion is merely stated here, but the figures and details of the method by which it is arrived at are given on page 244, in the section dealing with the thermo-chemistry of the cell.

Mixture versus Combination.

Adopting the double sulphation theory in as far as it is expressed by the statement that on discharge SO_4 passes out of the electrolyte and combines with both active materials at an equal rate, which rate is strictly proportional to the amount of current generated, the question as to the nature of the compounds it forms with them now remains to be considered. Gladstone and Tribe, when first enunciating the theory, distinctly took the view that in each case white lead sulphate was produced in admixture with an excess of unaltered lead or lead peroxide, and this has ever since been regarded as the stock explanation. Whatever else may be said for this belief, it certainly receives no support from the appearance or electrical behaviour of the discharged active materials. It is well known

that the distinctive opaque white colour of PbSO_4 cannot be detected, for during discharge the dark chocolate peroxide merely changes to a reddish brown hue, and the light grey spongy lead becomes a shade darker. Then, again, white lead sulphate is not, practically speaking, an active material at all when in a sulphuric acid electrolyte—that is to say, it is strongly resistant to electrolytic reduction or oxidation, whereas the active materials of discharged cells are desulphated on recharging with the greatest ease and rapidity, although sometimes containing as much SO_4 as corresponds to the presence of 50 per cent. of PbSO_4 .

To account for these anomalies it is said that the white sulphate is too finely divided to be individually distinguished, and that the apparent uniformity of discharged active material is really the resultant effect of a blend between the colours of its two separate components. The easy reducibility of the sulphate is also put down to the extreme intimacy of its admixture with the residue of more conductive material, although, oddly enough, when it has to be explained why some of the latter always remains unacted on even at the end of the most complete discharge, the non-conductivity and clogging effect of the sulphate is then made much of. The whole argument is indeed woefully inadequate. It receives little support from the appearance of actual mixtures of white sulphate with various proportions of porous lead or lead peroxide, nor from their behaviour when subjected to electrolysis, and the fact that, whenever a white sulphate can be observed in the active materials its inert electrical character is aggressively in evidence, directly contradicts it.

Having regard to the extreme difficulty, if not the impossibility, of reconciling the physical characteristics of discharged active materials with the assumption that they contain large percentages of normal lead sulphate in admixture with them, the chemical evidence bearing on this point becomes of considerable importance, and it is surprising to find how very little attention has been given to this aspect of the matter. By treating more or less discharged positive active material with dilute nitric and oxalic acids it may be entirely resolved—although in some cases only with difficulty—into soluble lead nitrate and an insoluble residue of normal

sulphate; and the amount of oxalic acid destroyed indicates how much peroxide was present. On the other hand, by treating it with a solution of ammonium acetate, the whole of the lead sulphate may—in theory, at any rate—be dissolved out and lead peroxide left behind. On the strength of analyses made on these lines, but not necessarily by precisely the same methods, the chemist expresses the composition of the active material in terms of so much peroxide and so much sulphate, and further maintains that it consists of a mixture of these two substances. In making the latter claim he goes too far, however, for it is possible to show that feeble compounds of lead peroxide and sulphate do exist, and that discharged positive active material behaves more like these than like a mere mixture.

It has been shown on page 214 that when lead peroxide is acted on by sulphuric acid in the presence of oxalic acid, it cannot be converted into normal sulphate, because the reaction stops short when the resultant substance approximates to the composition $\text{PbO}_2, 2\text{PbSO}_4$. Now this fact is of the greatest significance in the present connection, for it is difficult to believe that the peroxide would not be entirely decomposed by the oxalic acid without it were in true combination with the sulphate formed; and the reaction proceeds too rapidly at first, and the change to one of extreme slowness is too sudden, to be explained as due to the clogging effect of the latter. The compound produced is closely analogous in its character to red lead— $\text{PbO}_2, 2\text{PbO}$, which also is unaffected by oxalic acid owing to its peroxide being protected by its combination, in this case, with monoxide. The two present many other points of similarity. Both appear to be fairly stable as long as they can preserve their insolubility, but begin to break up when they can form soluble salts. Oxalic acid completely and instantly reduces red lead if nitric acid is present, and it attacks $\text{PbO}_2, 2\text{PbSO}_4$, but more slowly, under the same conditions. Solvents for lead monoxide, such as nitric or acetic acid, also set free lead peroxide, just as ammonium acetate accomplishes the same result by dissolving lead sulphate.

There is no reason to doubt that when lead peroxide is electrolytically reduced in a cell it undergoes the same changes as when chemically reduced by oxalic acid, and the behaviour of

thoroughly discharged positive active material towards reducing agents such as oxalic or sulphurous acids, as well as the fact that the discharge ceases long before all the peroxide has been destroyed, fully confirms this view. The variations of colour are also precisely alike in both cases. When half the peroxide has been reduced by oxalic acid and sulphated, the change of tint is barely perceptible, and far more alteration is experienced in passing to the two-third sulphation when it attains to the red-brown of a well discharged positive. Careful observation will generally show that the colour of positive electrodes remains much the same until nearly the end of the discharge.

So far, nothing has been said as to the nature of discharged negative active material. Physically considered, it is even more difficult to believe it to contain a large admixture of normal sulphate than it was in the case of the positive, but chemically it is not at all easy to prove the existence of a true compound. The Author has obtained some indications of a distinct limit to the sulphation of spongy lead when it approximates to the composition $\text{Pb}_3(\text{SO}_4)_2$ —that is, a two-third sulphation, as at the positive—but the results are hardly definite enough to put forward with certainty.

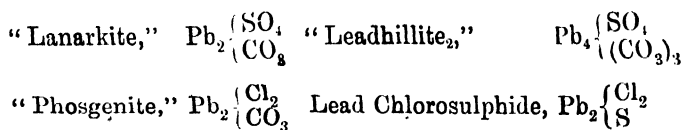
It may truly be said that, even if the case for the negative active material could be put on the same footing as the positive, the whole of the chemical evidence against the mixture theory would not, as yet, amount to much; but, considering the mental confusion to which that theory has given rise ever since its first promulgation, and the obstacles it presents to any rational explanation of the cell's working, there is every reason for rejecting it unless the chemist pushes his case home and proves, if he can, that the discharged active materials do in every respect behave as mixtures of two chemically distinct compounds. This he has never yet done, because he has been more interested in getting the two substances apart for the purpose of determining their relative quantities; and the degree of resistance they offer to separation has not appeared to him to be of any practical importance. This aspect of the matter is discussed more fully on page 231. Then, too, a preference naturally exists for expressing the results of a reaction in terms of a compound such as PbSO_4 .

which conforms to an exceedingly common and well-defined type, rather than in terms of sub-sulphates and peroxidised sulphates belonging to comparatively rare types that have been but little studied.

Polymerisation Theory of the Cell's Action.

Although the assumption that on discharge spongy lead and lead peroxide are directly converted into the compounds $\text{Pb}_3(\text{SO}_4)_2$ and $\text{Pb}_3\text{O}_2(\text{SO}_4)_2$ rather than into PbSO_4 is physically a far more tenable one, and a distinct step in the right direction, yet it does not enable one, to furnish a complete explanation of the behaviour of the lead cell, nor is it, in the Author's opinion, a full account of what really happens. His view of the matter is largely based upon the general characteristics of the lead compounds, and to ensure its full appreciation a few pages must be devoted to their consideration.

Lead, like all the metallic elements, unites with other elements and radicles to form normal compounds and salts of a perfectly definite composition, such as the monoxide, peroxide, sulphate, and so forth. It also enters with greater ease than most of the metals into more complex combinations to produce basic salts (sometimes termed sub-salts), in which it is partly combined with O or HO, as an oxide or hydrate, and partly with some other element or radicle. Usually it is capable of producing not merely one, but a whole series of basic salts with each radicle; of which the basic chlorides, nitrates, and acetates are well-known examples. In addition to this, it is almost unique amongst the metals in the facility with which it combines with two or more different radicles other than O or HO, and gives rise to curious compound salts, such as—



But besides all its normal, basic and poly-acid salts and compounds, lead will, under suitable conditions, form others which cannot accurately be represented by any formula at all.

The two most important commercial preparations of lead, namely white lead and red lead or minium, both furnish well-marked examples of this behaviour.

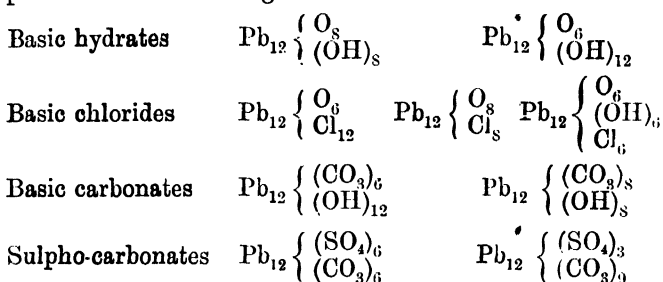
The first of these is a basic lead carbonate whose average composition when prepared by the old "Dutch" process is generally represented by the formula $2\text{PbCO}_3, \text{Pb}(\text{HO})_2$, or $\text{Pb}_3(\text{CO}_3)_2(\text{HO})_2$; but this is purely an approximation, as the relative proportions of carbonate and hydrate are found to vary very appreciably in different samples, even if produced under practically similar conditions. By other processes, especially precipitation methods, any number of basic carbonates of indefinite composition may be obtained, in which the proportions of CO_3 and HO vary over a much wider range, and show very little preference for uniting in any simple ratio such as is expressed by the formula just given.

Minium also has no fixed or definite chemical composition. Under the action of reagents it behaves as if it were composed of lead monoxide and lead peroxide, and the formula $2\text{PbO}, \text{PbO}_2$, or Pb_3O_4 , most nearly represents its average composition; but samples fully possessed of the fine scarlet colour—its distinctive physical property—have been found to approximate more closely to Pb_6O_7 , Pb_4O_5 , Pb_2O_3 , or to some other degree of oxidation between these simpler ratios.

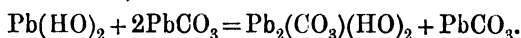
Now, Mendelejeff has ascribed some of the peculiarities of lead and its compounds (as also of boron, silicon, and other inorganic elements) to their "polymerisation." That is to say, he assumes that the molecule of lead may sometimes consist of a large but undetermined number of atoms, Pb_x ; while, in the same way, the molecule of lead monoxide is not necessarily composed of one atom of lead and one of oxygen, PbO , but of many multiples of these quantities, Pb_xO_x : so also lead peroxide may be Pb_xO_{2x} , and so on. The assumption does not, of course, affect the percentage composition of the lead compounds as ascertained by analysis, but only their molecular weights, and these cannot be directly determined.

This theory is partly based upon and affords a simple explanation of the readiness of lead to form the basic and poly-acids salts just referred to. Some of the atoms of lead in the complex molecule combine with one radicle and some with another; and if, solely for the purposes of illustration,

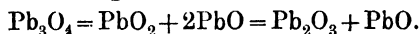
we suppose that there are twelve atoms of lead present, or that the molecule of lead monoxide from which they are derived has a composition $Pb_{12}O_{12}$, some of them may be expressed in the following formulæ :—



But the theory also equally well explains the real nature of the lead compounds of variable and indefinite composition. Their behaviour has always seemed somewhat puzzling, and they were at one time regarded as not being chemical compounds at all: merely intimate mixtures of other and simpler compounds. Thus, white lead was a mixture in varying proportions either of lead hydrate and normal lead carbonate, or of some definite basic carbonate with an excess of normal carbonate,



Red lead was a mixture of lead peroxide with lead monoxide, or possibly of lead sesquioxide with an excess of monoxide,



It will be evident, however, that we have only to assume a sufficiently complex molecular structure, and any number of true compounds between lead and a given set of radicles become theoretically possible—compounds of such closely-allied composition that their physical and chemical properties grade imperceptibly from each one to the next and so defy isolation. No doubt in some instances the whole series of compounds may be so unstable and so easily resolved into their proximate components that chemically they do appear to be nothing more than mixtures of them. In other cases only the combinations in simple ratios may possess much stability; but in every case the latter will probably be somewhat more stable and more readily formed

than the remainder, which may need special conditions for their production.

The manufacture of red lead furnishes a good example of the application of the theory, and a suggestive instance of the way in which a series of compounds is brought about and of the relationship of its various terms to each other. The further oxidation of litharge by roasting at a temperature not so high as that required for its own formation, does not appear to consist in the conversion of successive molecules of PbO direct to Pb_3O_4 , or some other definite oxide, but in the gradual absorption of oxygen by each molecule, which takes it up, atom by atom, and passes through a whole series of oxides of gradually increasing richness, the action proceeding more or less simultaneously and uniformly at all parts of the mass, according to the relative adequacy of the air supply. Again, supposing the constitution of the monoxide to be $\text{Pb}_{12}\text{O}_{12}$, the series of compounds obtained may be represented as follows; but fully to account for the observed facts, its molecular composition would have to be far more complex, so as to provide numerous other oxides between each of the terms shown:—

$\text{Pb}_{13}\text{O}_{12}$	12PbO	PbO
$\text{Pb}_{12}\text{O}_{13}$	$11\text{PbO} + \text{PbO}_2$	—
$\text{Pb}_{12}\text{O}_{14}$	$10\text{PbO} + 2\text{PbO}_2$	Pb_6O_7
$\text{Pb}_{12}\text{O}_{15}$	$9\text{PbO} + 3\text{PbO}_2$	Pb_5O_5
$\text{Pb}_{12}\text{O}_{16}$	$8\text{PbO} + 4\text{PbO}_2$	Pb_3O_4
$\text{Pb}_{12}\text{O}_{17}$	$7\text{PbO} + 5\text{PbO}_2$	—
$\text{Pb}_{12}\text{O}_{18}$	$6\text{PbO} + 6\text{PbO}_2$	Pb_2O_3

The first column gives the assumed molecular composition of the oxides; the second expresses it in terms of separate molecules of monoxide and peroxide as they would appear under analysis; and the third merely shows the simplest proportional composition. Most commercial minium comes somewhere between Pb_4O_5 and Pb_3O_4 , prolonged roasting generally being required to bring it quite up to the latter proportions; but as samples are occasionally found to be still further oxidised, the series is extended to the sesquioxide Pb_2O_3 . Here or hereabouts, the extreme limit to which the oxidation can be pushed by roasting is reached, because the temperature necessary to carry it to this stage is nearly as

high as that at which the deoxidation of the sesquioxide by heating commences. The two opposing tendencies balance each other and the absorption of oxygen then comes to an end.

It is this polymerisation theory which, in the Author's belief, furnishes the key to a true understanding of the chemical changes through which the active materials pass; which enables a complete reconciliation to be effected between their physical and chemical aspects; and which provides a full explanation of the electrical behaviour of the cell at all stages of its working and life.

In the first place, it is assumed, and everything that follows is based on this hypothesis, that the fully formed or charged active materials are not Pb and PbO_2 , but Pb_x and Pb_xO_{2x} ; that is not merely to say that the molecules are of a complex nature, physically considered, but that x atoms of lead are the smallest or unit number participating in any chemical reaction that may occur, so long as they preserve their polymeric structure intact.

On closing the external circuit, the molecules of lead at the negative begin to combine with SO_4 from the electrolyte, not, however, breaking up into independent molecules of normal lead sulphate, PbSO_4 , round a nucleus of uncombined metal; but the molecules as a whole taking part in the combination, and, as the discharge proceeds, passing through a continually changing series of sub-sulphates, without any rupture of their molecular complexity.

At the positive, the reactions, though different, take place in an exactly similar manner. Oxygen is gradually abstracted and SO_4 substituted in its place, a sequence of compounds of sulphate and peroxide being produced. Still keeping to our imaginary twelve atoms of lead to the molecule, these two series of compounds may be represented as follows:—

Pb_{12}	$\text{Pb}_{12}\text{O}_{24}$
$\text{Pb}_{12}(\text{SO}_4)$	$\text{Pb}_{12}\text{O}_{22}(\text{SO}_4)$
$\text{Pb}_{12}(\text{SO}_4)_2$	$\text{Pb}_{12}\text{O}_{20}(\text{SO}_4)_2$
$\text{Pb}_{12}(\text{SO}_4)_3$	$\text{Pb}_{12}\text{O}_{18}(\text{SO}_4)_3$
$\text{Pb}_{12}(\text{SO}_4)_4$	$\text{Pb}_{12}\text{O}_{16}(\text{SO}_4)_4$
$\text{Pb}_{12}(\text{SO}_4)_5$	$\text{Pb}_{12}\text{O}_{14}(\text{SO}_4)_5$
$\text{Pb}_{12}(\text{SO}_4)_6$	$\text{Pb}_{12}\text{O}_{12}(\text{SO}_4)_6$
$\text{Pb}_{12}(\text{SO}_4)_7$	$\text{Pb}_{12}\text{O}_{10}(\text{SO}_4)_7$
$\text{Pb}_{12}(\text{SO}_4)_8$	$\text{Pb}_{12}\text{O}_8(\text{SO}_4)_8$

But neither of these series is continued until the active material is fully sulphated and reaches the composition $\text{Pb}_{12}(\text{SO}_4)_{12}$, and it is possible to assign a direct physical reason why this should be so. Both lead and lead peroxide possess a very considerable electrical conductivity; but, on the other hand, pure lead sulphate is practically a non-conductor. The active materials must therefore undergo a great change of resistance in the course of their sulphation, a change either spread more or less uniformly over the whole discharge, or else occurring abruptly at some special stage. The latter appears to be what really happens, for although our information regarding the changes of resistance in lead cells is vague and meagre, we know that there is not much variation throughout the main portion of the discharge, but that the resistance begins to rise considerably towards the end; and whenever such a change of resistance takes place, it must necessarily terminate the discharge and bring about all the phenomena which do occur.

Just as fast as the resistance of the active materials, and therefore the internal resistance of the cell, rises, the potential difference at its terminals will fall away; and by the time the internal resistance has become very large in proportion to that of the external circuit, the potential difference will be reduced practically to zero. Or, to put it another way, just as fast as the resistance of the active materials rises, more and more of the electrical energy they would otherwise liberate is expended, so to speak, in their own molecules, until, when the rest of the resistances in circuit become relatively negligible, equilibrium is nearly established and the liberation of energy almost ceases. This is why it is impossible to push the discharge of a cell further, even by short-circuiting it; and yet on breaking circuit, *i.e.*, increasing the external resistance to infinity, the E.M.F. rapidly rises to nearly its original value.

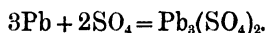
This way of regarding the changes taking place in the active materials is quite independent of what their precise composition may be when the alteration in their specific resistance takes place. When the Author first put forward these views in 1900 he thought the critical point most probably occurred at half sulphation, *i.e.*, Pb_2SO_4 and

$\text{Pb}_3\text{O}_4\text{SO}_4$, chiefly because this agreed best with the analyses of active material given in Ayrton's paper, and the maximum outputs for weight that can be obtained from them in pasted electrodes; but from experiments since made with chemically reduced peroxide, and described earlier in this chapter, he now has no doubt that for the positive active material it is two-third sulphation, $\text{Pb}_3\text{O}_4(\text{SO}_4)_2$, and a similar assumption, $\text{Pb}_3(\text{SO}_4)_2$, will also be adopted for the negative active material. That no more than half sulphation is observed in practice results no doubt from the impossibility of uniformly discharging the active materials, especially in such types of electrodes as best lend themselves to analysis and output for weight calculations, and the above figure is probably a mean between a two-third sulphation close to the support, and a considerably less than one-half sulphation at points most distant from it.

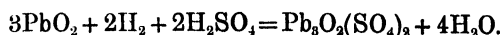
It is significant to note that, just as a thoroughly discharged cell will still give its full or nearly its full E.M.F. on open circuit, so, too, the action of oxalic acid, or similar reagents, does not cease when two-thirds of the peroxide has been reduced, but still proceeds with extreme and increasing slowness, showing apparently that the same chemical affinities are still at play, but now meet with some kind of internal resistance which hinders the change of composition they strive to bring about. In both cases, too, this great alteration in the rate of chemical action is not a gradual but an extremely sudden one.

The aggregate result, then, of the chemical changes at each electrode during a complete discharge are expressed in their simplest terms in the following equations:—

At the negative



At the positive



But when the active materials have attained to the above compositions, it only needs to augment the E.M.F. of the discharged cell ever so slightly from an outside source, and the point of equilibrium is passed; the active materials begin to absorb energy instead of liberating it, and incipient reversal commences. In fact, in primary battery language, the cell

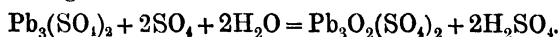
has polarised; but, unlike other cells, at both electrodes. (It is here assumed that the negative and positive electrodes contain equivalent amounts of active material, and both discharge under such equal conditions as regards maintenance of acid supply in their pores, &c., that they polarise or reverse at the same time.)

If the applied E.M.F. is increased sufficiently to maintain a current through the cell—which it will do at something between 1.5 and 2 volts—full reversal then sets in. At the negative, lead is directly peroxidised; and at the positive, peroxide is directly reduced to metal, the proportion of sulphate remaining constant throughout; and the two series of compounds through which the active materials may be presumed to pass are given below, commencing with the two last terms of the previous series, which represented their composition at the end of a complete discharge.

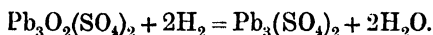


In this way the composition of the two active materials is exactly transposed; and, as their complex molecular structure is maintained throughout the reversal, their electrical conductivity is never interrupted, but simply remains at the comparatively low value to which it had been reduced at the end of the discharge. The following equations give the sum of the reactions during a complete reversal in the simplest terms.

At the negative



At the positive



As the nett result of these reactions is nothing more than an interchange of compounds between the anode and cathode, the cell neither furnishes an E.M.F. during this stage nor should it, in theory, require one to be impressed on it to effect the reversal, for its potential energy is no greater at the end than at the beginning of the process. The whole of the

energy, therefore, that is expended during reversal is required to overcome the cell's inertia, or, electrically considered, its internal resistance and polarisation; and the whole of it is dissipated as heat in the cell itself.

As soon as all the lead has been oxidised at the one electrode and all the peroxide reduced at the other, the reversal proper is finished, the cell develops an E.M.F. in the opposite direction to that it first possessed, and recharge commences; but as the quantity of SO_4 then begins to diminish in both active materials, their conductivity goes up rapidly and the end of the reversal is consequently not marked by so much increase in the P.D. required to maintain the flow of current as might be expected.

The reactions on recharge are, of course, *exactly the same* whether they follow upon a reversal or, as is more usual, merely upon discharge, the difference being that the E.M.F., direction of current flow, and composition of the active materials are reversed. In either case they consist in the abstraction of SO_4 from both active materials until they are brought back to lead and lead peroxide just as they existed at the commencement of the discharge. The series of compounds through which this will be effected are similar to those of discharge, but now occurring in the converse order, and they are given below, the hypothetical molecules containing 12 atoms of lead still being presumed.

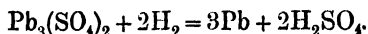
$\text{Pb}_{12}\text{O}_3(\text{SO}_4)_8$		$\text{Pb}_{12}(\text{SO}_4)_8$
$\text{Pb}_{12}\text{O}_{10}(\text{SO}_4)_7$		$\text{Pb}_{12}(\text{SO}_4)_7$
$\text{Pb}_{12}\text{O}_{12}(\text{SO}_4)_6$		$\text{Pb}_{12}(\text{SO}_4)_6$
$\text{Pb}_{12}\text{O}_{14}(\text{SO}_4)_5$		$\text{Pb}_{12}(\text{SO}_4)_5$
$\text{Pb}_{12}\text{O}_{16}(\text{SO}_4)_4$		$\text{Pb}_{12}(\text{SO}_4)_4$
$\text{Pb}_{12}\text{O}_{18}(\text{SO}_4)_3$		$\text{Pb}_{12}(\text{SO}_4)_3$
$\text{Pb}_{12}\text{O}_{20}(\text{SO}_4)_2$		$\text{Pb}_{12}(\text{SO}_4)_2$
$\text{Pb}_{12}\text{O}_{22}(\text{SO}_4)$		$\text{Pb}_{12}\text{SO}_4$
$\text{Pb}_{12}\text{O}_{24}$		Pb_{12}

The total effects of the recharge, expressed in their simplest terms, are as follows:—

At what was the negative before reversal, but now the positive,



At what was the positive before reversal, but now the negative,



It is very remarkable that the process of reversal should have been entirely ignored by all writers on the chemistry of lead cells, for not only is the enquiry as to how electro-positive lead can be converted into electro-negative lead peroxide one of extreme interest in itself, but it also provides a searching test by which to decide as to the real character of the active materials; and under it the idea that white lead sulphate can be the normal discharge product gives way altogether.

Interpreting that view in the most favourable light, the active materials at the end of a discharge consist of an underlying structure of conductive lead and lead peroxide respectively, still in electrical connection with their supports, but surrounded and choked by an equal quantity of an insoluble non-conductive substance which largely cuts it off from contact with the electrolyte and is the sole cause of the fall in the P.D. of the cell. Under these circumstances, when the reversal commences, the applied E.M.F. can but be spent in overcoming the internal resistance due to this state of affairs, and enabling the residue of hitherto unattacked material to continue sulphating till practically the whole of it is converted into normal sulphate. That this does not happen is palpable to the eye, but, assuming for the nonce that white sulphate in intimate admixture with itself can produce greyness and brownness, even then its continued reduction and peroxidisation under such conditions would remain totally unaccounted for. The latter argument equally applies if the far less likely assumption is made that at the end of the discharge the sulphate formed has cut off the remaining lead and lead peroxide from all electrical connection with their supports. The reversal, if it went on at all, could only do so extremely slowly, whereas in practice far larger currents can be absorbed during reversal without a trace of gas showing than during any period of ordinary recharge.

No doubt the idea that on reversal both active materials have to be converted into normal sulphate before they can undergo further reduction or oxidisation may receive apparent

support from the very evident formation of white sulphate that often accompanies that process, especially if the active material is present in considerable masses, but this is due to excessive local action, and any electrode in which the active material is distributed in thin layers may be reversed without the slightest sign of "sulphating," provided a sufficiently heavy current is continuously maintained.

There is, moreover, some direct evidence as to the real nature of reactions on reversal, for it has been frequently noted that traces of lead peroxide make their appearance on the surface of negative active material towards the end of its complete discharge. In practice this is most probably brought about by a reinforcement of the cell's E.M.F. from others not so fully discharged, in series with it, but that does not affect the value of the observation itself, which lies in showing that the reversal commences with the formation of lead peroxide long before the active metal is fully sulphated. If the mixture theory held good, such a reaction would imply either that it was possible for the electrolytic action to be diverted to the peroxidisation of an inert substance like normal lead sulphate while metallic lead yet remained in the circuit, or else that metallic lead could be directly peroxidised at the end of a discharge although it only sulphated at the beginning; and it is difficult to say which of the two alternatives seems most incredible.

Even putting aside the reversal, the condition at which the active materials are usually supposed to have arrived at the end of a discharge renders the possibility of a recharge equally unthinkable. Although so thoroughly porous that their every molecule is reached by the electrolyte, they are not composed of a number of separate grains in close juxtaposition, but possess a continuous structure. How, then, is it possible for as much as every other molecule to be converted into an entirely distinct non-conducting substance without immensely deteriorating the mechanical and electrical continuity of the active materials, and this having taken place, by what means are they brought within reach of the current and restored to their original condition on recharging.

The constitution of the active materials under all normal conditions of usage has now been examined, and it has been

shown, by the aid of the hypothesis of polymerisation, that at every stage they may consist of homogeneous and conductive chemical compounds, whose proximate composition, except when fully charged, is most conveniently expressed by saying that they appear to be a combination of normal lead sulphate with lead or lead peroxide; or, during the period of reversal, with both at the same time. From the very nature of these compounds it is evident that each one of them cannot be actually separated from its fellows. The most that can be expected is a demonstration of the existence of the series as a whole, and of a few compounds occupying special positions in it. Evidence in favour of one of the latter— $\text{PbO}_2, 2\text{PbSO}_4$, the limiting term between the end of the discharge and the commencement of the reversal—has already been dealt with on page 218; and it seems possible that others may eventually be individualised in a like manner.

Because lead sulphate can be extracted from partially or fully discharged active materials by solvents such as ammonium acetate, it has been said that it must be in admixture, but, on the contrary, this very result, if carefully examined, furnishes the most direct testimony that it is really in combination. A solution of ammonium acetate of given strength will dissolve a definite amount of lead sulphate quite independently of whether or no it is an admixture with some other insoluble substance. The latter might possibly retard the rate of solution somewhat, but in the end the result would be the same. When, however, the proper quantity of acetate solution is applied to lead peroxide, chemically reduced and sulphated, it will no longer dissolve out anything like the whole of the sulphate. A good deal is extracted, but it is doubtful whether it can all be removed, even by any reasonable excess of acetate, if it is employed all at one time; and to accomplish this result it must be used in several portions, or, better still, the peroxide must be continually washed with fresh solution. If, instead of trying to remove the lead sulphate and leave the peroxide, the reverse operation is attempted by means of nitric and oxalic acids, similar behaviour will be observed, although, owing to the more powerful nature of the solvents, the two may then be separated more easily when so desired. Other instances of the difficulty of freeing one substance from

another, which by itself very freely dissolves in the solvent employed, are of constant occurrence in practical chemistry, and they always point to some degree of combination. An instructive example, specially applicable to the present case, occurs in the preparation of lead peroxide from red lead by dissolving out the monoxide with dilute nitric acid.

An obvious objection to any theory involving the formation of numerous lead compounds of indefinite composition is that it runs counter to the usual text-book chemistry, which draws an absolutely hard-and-fast line between chemical compounds and mechanical mixtures, and arbitrarily allots to one class or the other anything which may seem to fall between them. If there is any force in this view of the matter it equally applies, of course, to many other lead compounds besides the special sulphated ones now under consideration, for it has already been shown what a marked tendency they all have to depart on the slightest provocation from the rules laid down as to how they should behave. Of recent years, however, the rapid advances made in our knowledge of physical chemistry have provided much evidence, obtained from very different sources, all tending to prove that substances may exist whose components do not apparently follow the law of combination in multiple proportions, and yet must in other respects be regarded as very different to mechanical mixtures. Even the old distinction between "atomic" and "molecular" compounds is giving way, and the latter are coming to be accepted merely as one of the many intermediate stages between the two extreme limits.

It only now remains to consider the causes which give rise to certain conditions of the active materials in which their normal conductivity is seriously lessened or partially interrupted, and which lead up to the appearance of the white irreducible sulphate.

With ideal electrodes the end of a discharge would be determined by the whole of their active material just beginning to pass into that phase of their composition which is accompanied by a high and rapidly increasing specific resistance, for the P.D. then falls sufficiently to render any further useful output impossible. If the recharge is at once commenced, a very small abstraction of SO₂ suffices to restore

the active materials to the conductive state, and the changes wrought by the charging currents are again shared equally between their every part, until finally all complete their desulphation at the same time.

In practice, the energy of discharge and recharge can never be quite uniformly withdrawn from or supplied to the active materials even of the best designed electrodes, while with most of them the inequality will be considerable under ordinary conditions of working; and if the discharge is prolonged to its utmost limits, some parts, although not much more sulphated than the remainder, will attain to a far higher specific resistance. On recharging, the least sulphated portions soon regain their conductivity, but the difference of resistance between these and those most fully discharged then becomes so pronounced that, automatically, the latter are almost cut out of the circuit. The small fraction of current that does pass through them may eventually bring them round, but they will lag so much behind the remainder that if the recharge is cut fine by stopping at too low a P.D. limit, merely because gas is being evolved, or because as many ampere hours have been put back as were previously withdrawn, they can have no chance of being properly desulphated. This constitutes the beginning of abnormal sulphation.

It is only necessary to imagine a few discharges and recharges on these lines to see that some of the active material will soon acquire such a high resistance that the charging current fails to attack it at all, and it remains permanently sulphated; and if the electrodes are of faulty design, or if the injurious treatment is accompanied by high rates of discharge and recharge which greatly accentuate the inequalities of current distribution, more and more of the active material may get out of step, until only a thin layer in direct contact with the support is left in an effective condition. The output will, of course, be steadily shrinking all this while, accompanied by a proportionate reduction in the length of time required for charging.

Although the material affected no longer forms part of the main electrolytic circuit, it can still be chemically attacked by local action with any reducing or oxidising agents that may

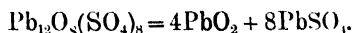
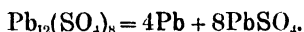
be present in the electrolyte. The action will be extremely slow owing to the protective effect of the large percentage of sulphate already in combination, but the results will be culminative. Unfortunately, most impurities commonly found in a cell are capable of undergoing alternate oxidation and reduction, and can therefore pass by diffusion between the electrodes and attack each active material in turn, so that the merest traces may do an unlimited amount of mischief if sufficient time is allowed them. In this way, at the positive, arsenious acid can be converted into arsenic acid; ammonia through various intermediate stages to nitric acid; hydrochloric to hypochlorous and chloric acids; ferrous sulphate to ferric sulphate; manganous sulphate to permanganic acid, and so on. At the negative, all these changes can take place in the reverse direction to that mentioned, but with some of them the oxidation proceeds easiest, with others the reduction.

Even if every extraneous substance could be excluded from a cell, there yet remain persulphuric acid and hydrogen peroxide, which can certainly act as strong oxidising agents, and the latter probably also behaves as a reducing agent towards lead peroxide. It is true that these two, unlike the others, are themselves destroyed in the act, but then they are almost certainly renewed to some extent with each recharge.

In every case local action will be far more dangerous in a discharged than in a charged cell, for in the latter the desulphated active material will be first attacked and no harm will be done beyond a reduction of output on the next discharge, and this is one reason why cells should not be allowed to remain uncharged longer than can be helped; but if a cell has been not only fully discharged but partially reversed by others of larger output in series with it, delay in recharging must be still more harmful, for then the most sulphated portions of the active materials will contain both lead and lead peroxide, and these will mutually react till one or the other is eliminated. On this account the circuit should never be interrupted while a reversal is being carried out, and even then it is almost impossible to reverse many types of electrodes without excessive local action ensuing, and portions of the active materials becoming so heavily sulphated that they cannot be freed from it again. In these various

ways over-sulphation of the active materials proceeds, and might, it would be thought, so continue until the whole of the lead or lead peroxide in the parts affected had been attacked, and normal sulphate, PbSO_4 , finally remained. But, judging by the difficulty that is experienced in pushing sulphation to this extreme limit when operating on the active materials with chemical reagents outside the cell, it seems probable that the white sulphate is produced in a different manner. Although great emphasis has been laid on the need for recognising that the lead sulphate formed on discharge is normally in true combination with the rest of the active material, it is fully admitted that their chemical behaviour proves these compounds to be but feeble and unstable ones. It seems extremely likely, therefore, that under certain conditions they break up in the cell itself, and that herein lies the real origin of "sulphating" in its most pronounced form. The molecules of active material forsake their allotropic and polymeric structure and are resolved into what, from a general chemical standpoint, would be termed a more normal state, but one which in its special relationship to storage cells must here be termed abnormal. Each complex molecule splits up into a number of simpler ones, some of normal sulphate and others of lead or lead peroxide.

Taking, for example, the composition of the fully discharged active materials as represented by the two terms previously given, these would break up as follows:—



The results that might be predicted from such a change closely accord with those actually characteristic of "sulphating." The rearrangement of structure could hardly be accomplished without producing some alteration in the density of the active materials, and it is most probable that the independent molecules will require more room than when in a combined state. A strain is thus put upon the active materials which leads to their disintegration, unless it can be taken up internally by a reduction of porosity; and, if the sulphation is excessive, the effect extends to the support which either expands, buckles, or bursts asunder. The molecules of Pb

and PbO_2 , isolated from the electrolytic circuit by the surrounding sulphate, themselves soon become sulphated by local action, and so visible patches of white irreducible sulphate soon make their appearance. In all probability such a modification of structure cannot occur unless the active materials are already considerably over-sulphated. It may then be inevitable without further cause, or, on the other hand, it may need some special condition to bring about the final rupture.

Thermo-Chemistry of the Cell.

The researches of Joule into the relations of heat to other forms of energy, and his determination of its mechanical equivalent, rendered it possible to express in terms of mechanical and electrical units the heat liberated or absorbed by chemical combinations or decompositions. The quantity of heat required to raise the temperature of 1 gramme of water 1°C .—the unit of heat, or “calorie”—represents the same amount of energy as 43,000 gramme-centimetres or 4.24 volt-coulombs or “joules,” and these constants are termed Joule’s equivalent or coefficient. In more practical units a calorie is equal to 3.1 foot-pounds or 0.00117 watt-hours.

In 1851 Sir William Thomson, now Lord Kelvin, applied Joule’s data to the reactions taking place in galvanic and electrolytic cells, and showed how their E.M.F. could be theoretically calculated. The work done by or upon a cell is evidently the product of its developed or applied E.M.F. and the quantity of electricity passed through it. That is to say,

$$W = QE,$$

where W is the work in watt-seconds or joules, Q the quantity of electricity in ampere-seconds or coulombs, and E the E.M.F. in volts. Presuming that the whole of this work (apart from losses due to internal resistance) is derived from or expended in electro-chemical changes, its amount can also be stated in different terms by considering the energy that would be dissipated as heat should the separated ions recombine chemically and reproduce the original compound or compounds. To avoid complications, the simplest case of electrolysis, in which the two ionic components of a compound

are directly liberated at their respective electrodes, will be assumed.

If H represents the calories evolved by the recombination of unit weight of either one of the separated ions, and e its electro-chemical equivalent—that is, the quantity of the ion set free by a unit or coulomb of electricity, then eH is the heat generated by the recombination of the same quantity of the ion, and JeH is the electrical equivalent of that heat in watt-seconds, J being Joule's coefficient. But Q coulombs having passed through the cell, Q times as much of the ion will have been liberated, and Q times as much energy would result from its recombination, so

$$\begin{aligned} W &= QJeH, \\ \text{also } QE &= QJeH, \\ \text{and } E &= JeH. \end{aligned}$$

Now, the electro-chemical equivalent of any ion may be derived by multiplying its chemical equivalent or combining weight, c , into the electro-chemical equivalent, h of hydrogen, which is 0.00001088 grammes per coulomb; so $e = hc$, and

$$\begin{aligned} E &= JhcH, \\ &= 4.2 \times 0.00001088 \times cH, \\ &= 0.0000436cH. \end{aligned}$$

This formula is of no use unless the value of H is known for whatever compound may be under consideration, but within recent years it has been experimentally determined for most of those reactions which are met with in practical electro-chemistry. If, as is usually the case, the action in the cell involves a simultaneous decomposition and combination—perhaps several of each— cH is then the algebraical sum of all its individual values.

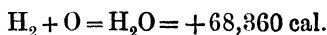
When discussion first commenced in the early eighties as to the true nature of the discharge reactions in lead cells, the heat of formation of lead preoxide was not then known, and consequently a determination of the discharge E.M.F. by means of Thomson's law—as the above equation is termed—could not be made until Tschelltzow ascertained its value in 1885. He also calculated the E.M.F. of the cell, and showed with approximate correctness that only on the supposition of double sulphation on discharge could a figure be obtained.

which at all agreed with actual observations ; but, for one reason or another, this evidence is generally treated, especially by those who dispute the conclusion to which it leads, as of little or no importance.

Thomson's law is based on the supposition that in a reversible cell of infinitely small internal resistance the whole of the energy of chemical combination can be converted into electrical energy in the external circuit, and vice versa. It has, however, been shown by Helmholtz and others that, for thermo-dynamical reasons, the law can only be strictly correct when the E.M.F. of the cell is independent of the temperature : if it decreases with an increase of temperature, then some of the chemical energy appears as heat ; but if the E.M.F. rises with the temperature, then heat is withdrawn from the surrounding medium and converted into electrical energy in addition to the energy of chemical combination, and the cell becomes cooler on discharge. In either case a corrective term, expressing the rate of variation of E.M.F. with temperature, has to be added to Thomson's equation, as it is evident that a number of different E.M.F.s cannot be derived from a formula all of whose members are fixed quantities ; for heats of combination, H , remain practically the same within ordinary temperature limits. A Daniell cell is generally quoted as one of the best examples of the calculation of an E.M.F. by means of heats of formation. The cell has a positive temperature coefficient, *i.e.*, its E.M.F. rises on heating, but so small in amount—about 0.00003 volt per degree Centigrade—that it only represents a departure from Thomson's equation of about 1 per cent. at ordinary temperatures. The temperature coefficient of a lead cell is a rather uncertain quantity, for it varies considerably with comparatively small changes in the strength of its acid electrolyte. The investigations of Preece, Streintz, and Dolezaleck, all show, however, that under normal conditions it is positive and, at most, of the same order of magnitude as that of a Daniell cell, probably much less, so there appears to be no need to attempt to introduce temperature corrections when calculating the E.M.F. of a lead cell, especially as the thermo-chemical data employed are admittedly not capable of a very high degree of accuracy.

The bulk of the determinations of heats of combination have been made by J. Thomsen and by M. Berthelot. The figures obtained by the former are published in his "*Thermo-chemische Untersuchungen*" (1882-1886), but the more important of his results are available in English in a book by Pattison Muir entitled "*The Elements of Thermal Chemistry*." A great many of Berthelot's figures are to be found in his "*Essai de Mécanique Chimique*" (1879), but in the second volume of his "*Thermochimie*" (1897) he has collected the determinations made by himself, Thomsen and numerous other scientists. A large number of additional figures are constantly being obtained, and may be found scattered throughout the various publications and journals dealing with chemistry and physics.

Heats of formation are mostly given in terms of the calories liberated by one formula weight (in grammes) of the resultant compound. For example,



means that 68,360 calories are generated when two grammes of hydrogen combine with 16 grammes of oxygen to form 18 grammes of water.* In thermo-chemical notation, however, this formula is generally abbreviated by merely putting

* For many purposes it has been found more convenient to reduce all heats of formation to terms of the calories evolved by the combination of as much of the substances as would react with a single combining weight (in grammes) of hydrogen or its equivalent. The general relationship between the two systems may be expressed thus:—

$$\text{Calories of grammes equivalent} = \frac{\text{calories of formula weight}}{\text{valency}}.$$

The heat of formation of a formula weight of a monovalent compound such as [H,Cl], will therefore remain unaltered for a gramme equivalent; but if bivalent it will be divided by 2, if trivalent by 3, and so on. For instance, the heat of formation of water will then be stated as 34,180 cal. instead of 68,360 cal., and the former figure indicates the heat generated by the union of 1 gramme of hydrogen with 8 grammes of oxygen.

Another modification of nomenclature sometimes employed is to express heats of formation in terms of the amount of heat required to raise the temperature of 1 kilogramme—instead of 1 gramme—of water 1°C. Most of Berthelot's results are given in this form—for example, $[\text{H}_2\text{O}] = 68.36 \text{ cal.}$ —and this unit of heat is called the large calorie or kilocalorie, in contradistinction to the small calorie generally employed by Thomsen, and which has been adopted here.

commas between the symbols of the combining substances and enclosing the whole in a square bracket thus

$$[\text{H}_2, \text{O}] = 68,360 \text{ cal.}$$

The same compound may have several different heats of formation, according to the materials from which it is prepared.

$$[\text{H}_2, \text{S}, \text{O}_4] = 192,980 \text{ cal.}$$

is the heat of formation of 98 grammes of sulphuric acid by the union of 2 grammes of hydrogen, 32 grammes of sulphur and 64 grammes of oxygen ;

$$[\text{H}_2, \text{O}, \text{SO}_3] = 89,680 \text{ cal.}$$

its heat of formation from 2 grammes of hydrogen, 16 grammes of oxygen and 80 grammes of sulphur trioxide ; and

$$[\text{H}_2\text{O}, \text{SO}_3] = 21,320 \text{ cal.}$$

its heat of formation from 18 grammes of water and 80 grammes of sulphur trioxide. \

The symbol Aq is used to indicate a very considerable but indefinite quantity of water when solutions are being dealt with. For instance,

$$[\text{H}_2\text{SO}_4, \text{Aq}] = 17,860 \text{ cal.}$$

represents the "heat of solution" or heat evolved when 98 grammes of pure acid are largely diluted with water.

Most compounds evolve heat in their formation, and are called "exothermic," but a few which absorb heat are termed "endothermic," and this behaviour is indicated by placing the negative sign before the number representing the heat so taken up.

$$[\text{H}_2\text{O}, \text{O}, \text{Aq}] = -23,060 \text{ cal.}$$

shows that 23,060 calories are absorbed during the combination of 16 grammes of oxygen with 18 grammes of water to form a solution of 34 grammes of hydrogen peroxide in a large quantity of water.

The negative sign is also employed, but on both sides of the equation, to express the decomposition of an ordinary exothermic compound, and

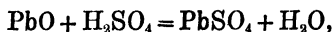
$$- [\text{PbO}, \text{O}] = -12,000 \text{ cal.}$$

stands for the heat taken up in decomposing 289 grammes of lead peroxide into lead monoxide and oxygen.

When an endothermic compound is destroyed, the negative sign appears in front of the symbols only, for energy is then *liberated*, so the resolution of 48 grammes of ozone into normal oxygen is represented by

$$- [O_3, O] = 29,000 \text{ cal.}$$

When a number of combinations and decompositions are involved in the same reaction they are merely written in sequence with the appropriate sign before each, and the net heat of formation of the whole of them appears on the other side of the equation. For instance, the reaction of dilute sulphuric acid with lead monoxide, according to the ordinary chemical equation



will be represented by the thermo-chemical equation

$$[PbO, SO_3] - [H_2O, SO_3, Aq] = 62,670 - 39,170 = 23,500 \text{ cal.}$$

Reverting to Thomson's formula, the application of heats of formation to calculations of E.M.F. is very simple, because the figures directly represent either CH or $CH \times \text{valency}$, according as they are given in terms of a gramme equivalent or a formula weight. The latter system being used here,

$$E = \frac{0.0000436 \times \text{heat of formation in calories}}{\text{valency}},$$

and as applied to lead cells, where all the reactions are bivalent,

$$E = \frac{0.0000436 \times \text{heat of formation in calories}}{2}$$

$$= \frac{\text{Heat of formation in calories}}{46,000}.$$

That is to say, a net heat of formation of 46,000 cal. corresponds to 1 volt, and the E.M.F. of the cell may be arrived at by dividing the heat resulting from the whole of the reactions taking place by 46,000.

Before proceeding to calculate the E.M.F. of a lead cell by means of this relationship, it must be decided with which E.M.F., it is to be compared when obtained, for the cell has many. Most of them, however, are transient and variable E.M.F.s due to degrees of liquid polarisation and to gaseous concentration on recharge, as well as to the

presence of unstable compounds, which cannot be ascertained and allowed for in the calculations; and when these have all been eliminated there remains, in all probability, only one true E.M.F. for any given strength of acid. It may be that even with an absolutely constant electrolyte the E.M.F. does vary slightly according to the stages of discharge or sulphation of the active materials; and should this be so, the E.M.F. furnished by nearly or entirely desulphated active materials will best correspond with the

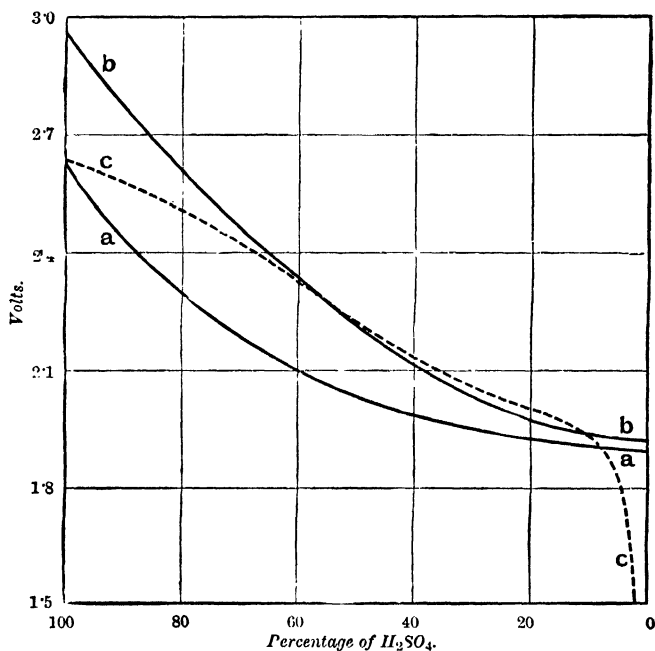


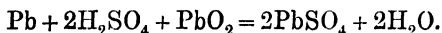
FIG. 156.—Curves of Variation of E.M.F. with Strength of Acid.

reactions assumed in the thermo-chemical equations. As a standard of comparison in the present instance, Gladstone and Hibbert's determinations of the E.M.F. of fully-charged electrodes in various strengths of acid will be adopted. Part of their results have already been given in curve *b*, Fig. 129, but the whole of their readings are embodied in the dotted curve *c*, Fig. 156. Most of their values for the higher

percentages of acid were obtained with only the peroxide plate in the strong acid, on account of the excessive local action to which the spongy lead of the negative would otherwise have been subjected, so these figures have had to be corrected for both plates in the same strength of acid from the data they themselves furnish giving the E.M.F. between two plates of plain lead in different strengths of acid.

It now remains to prepare a curve of calculated E.M.F.s to compare with this curve, based on observation.

The general chemical equation for the discharge reactions, in accordance with the double sulphation theory, is



The corresponding thermo-chemical equation will be

$$2[\text{Pb}, \text{SO}_4] + 2[\text{H}_2, \text{O}] - 2[\text{H}_2, \text{SO}_4] - [\text{Pb}, \text{O}_2] = 121,000 \text{ cal.}$$

$$225,940 \quad 136,720 \quad 179,360 \quad 62,300 = 2.63 \text{ volts,}$$

if the electrolyte is undiluted sulphuric acid, and

$$2[\text{Pb}, \text{SO}_4] + 2[\text{H}_2, \text{O}] - 2[\text{H}_2, \text{SO}_4, \text{Aq}] - [\text{Pb}, \text{O}_2] = 85,300 \text{ cal.}$$

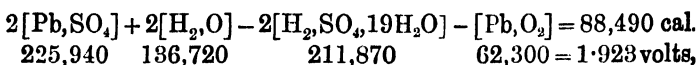
$$225,940 \quad 136,720 \quad 179,360 \quad 62,300 = 1.855 \text{ volts,}$$

if it is very dilute acid.

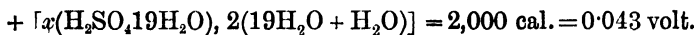
These two equations provide the figures for the extreme limits of the curve, and by replacing $[\text{H}_2, \text{SO}_4]$ or $[\text{H}_2, \text{SO}_4, \text{Aq}]$ by $[\text{H}_2, \text{SO}_4, \text{H}_2\text{O}]$, then, by $[\text{H}_2, \text{SO}_4, 2\text{H}_2\text{O}]$, and so on, any number of intermediate values can be interpolated between them. Curve *a*, Fig. 156, shows the result, and it is very evident that it does not agree at all well with curve *c* except at two points, one corresponding to a 7 per cent. solution (specific gravity 1.050) and the other to 100 per cent.—that is, pure acid; and, for reasons which will be given directly, it seems most unlikely that this coincidence is other than accidental.

But, as the Author pointed out in 1894, the thermo-chemical equation from which curve *a* is constructed does not take count of every source of E.M.F., although it includes all those usually considered. This may best be made clear by considering some specific point on the curve, and the one will be selected which represents the E.M.F. when the electrolyte has a specific gravity 1.160, and

corresponds to the composition $\text{H}_2\text{SO}_4, 19\text{H}_2\text{O}$. In this case the thermo-chemical equation is



and, on comparing it with the corresponding equation just given for undiluted acid, it will be observed that, when $2\text{H}_2\text{SO}_4$ is withdrawn from the electrolyte by the sulphation of the active materials, its previous heat of dilution with $2 \times 19\text{H}_2\text{O}$ is properly debited, and the resultant heat of formation is diminished by that amount, *i.e.*, 32,500 cal. What has been overlooked, however, is that these 38 molecules of water, plus the two additional molecules which take the place of the acid, do not remain altogether inactive, but go to further dilute the rest of the electrolyte, and so liberate a small amount of energy, which has to be added to the nett total. The additional term is



$x(\text{H}_2\text{SO}_4, 19\text{H}_2\text{O})$ stands for the bulk of the electrolyte, which should be in sufficient quantity not to have its strength appreciably reduced by further dilution with, in this instance, 40 molecules of water, and so x must be some large number.

The calculated E.M.F., then, of a cell containing a 22.3 per cent. solution of sulphuric acid will be 1.923 volts plus 0.043 volt = 1.966 volts, while the observed value, according to Gladstone and Hibbert's figures, is just 2.0 volts.

The above correction is not a constant, because not only do the number of molecules of water available for further dilution of the electrolyte vary with its strength, but the avidity of sulphuric acid for water is also continually altering according to the quantity with which it has already combined. For instance, in the extreme case of concentrated acid it is apparent that the only water here liberated is the two molecules resulting from the main discharge reactions, but these dilute the rest of the acid to such good effect that energy corresponding to an additional 0.32 volt is evolved. In the other extreme of an excessively dilute electrolyte hardly any more energy can result whatever further quantity of water is added, and consequently the correction becomes almost nil, but down to a 6 per cent. solution—the point at which

the E.M.F. commences to fall rapidly—it is still sufficiently large to be worth considering. The curve given in Fig. 157 shows the heat evolved by diluting pure acid to any degree down to about a 5 per cent. solution, and from this can be calculated the necessary addition of E.M.F. for a sufficient number of points on curve *a*, Fig. 156, in order to construct curve *b*, which gives the true calculated E.M.F. of the cell for all strengths of acid.

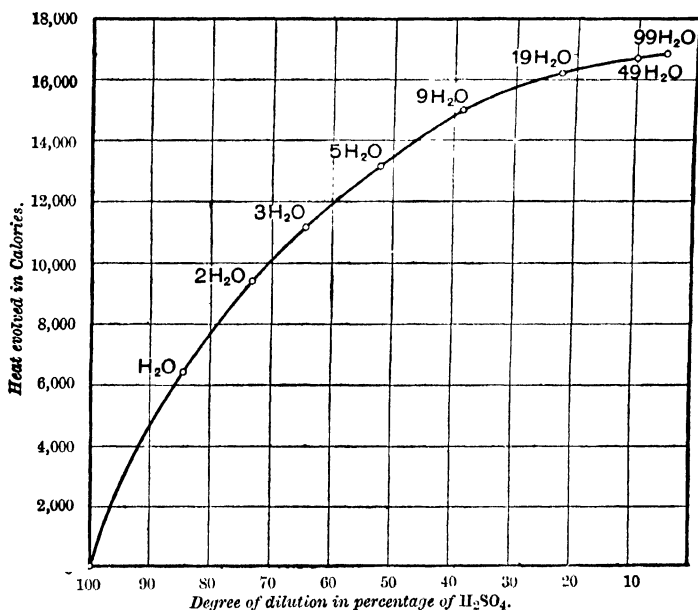


FIG. 157.—Heat of Dilution of Sulphuric Acid.

Between the limits of about an 8 per cent. to a 60 per cent. solution (specific gravities 1.05 to 1.50, which far more than cover the range of strengths ever employed in practical cells) curves *b* and *c* are almost coincident, the observed results being but slightly higher than those calculated, for the example worked out above shows the maximum divergence of less than 0.04 volt; and in view of this agreement it seems difficult to resist the conclusion that the double sulphation theory does receive unqualified support and confirmation from the thermo-chemical data.

For very weak acid solutions the two curves rapidly diverge, but it can be freely admitted that here the double sulphation is beginning to break down and its thermochemical equation no longer holds good. For strong acids, above 60 per cent., a considerable discrepancy also manifests itself, but in all probability it is the observed figures that are now at fault. It has already been mentioned that none of these readings could be taken with the spongy lead electrode in the strong acid because of the excessive local action, and in every case either a plain lead negative had to be directly substituted or else the reading corrected from another in which plain lead had been used. Now there is no reason to suppose that the tendency to local action is diminished by this alteration, but the solid lead only exposing such a small surface to the electrolyte is immediately covered with a thin film of sulphate, and so protected from further attack. In other words the negative used is of infinitesimal capacity but fully discharged, and it may well be that under such conditions it is impossible to measure the true E.M.F. by ordinary methods.

It may be thought that the very success with which the E.M.F. of a lead cell can be thermo-chemically calculated is in itself an argument against those views, upon which the Author has laid considerable stress, as to the polymeric condition of the active materials and the special sulphated compounds they form on discharge, because none of these things are allowed for in the equations; but it does not at all follow that their existence need produce any material difference in the various heats of formation. Certainly the way in which spongy lead negatives oxidise when exposed to the air—so fast indeed that the whole electrode becomes quite hot—suggests an unusual combining energy, but on consideration it seems doubtful whether the extreme porosity of the active material, the fact that the atmosphere has direct access to *each individual molecule* of it, does not afford a complete and simple explanation of the phenomena as one of an increase in the *rate* rather than in the *intensity* of combination. Even should the allotropic state be accompanied by an exaltation of chemical affinity, both electrodes are assumed to be equally affected, and, so far as the resultant

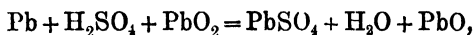
E.M.F. of the cell was concerned, the eagerness with which the spongy lead acquired oxygen would be neutralized by the unusual reluctance with which the lead peroxide gave it up.

Before leaving the subject of the exact interpretation to be placed on the thermo-chemical equations it will be advisable to explain two points which might, at first sight, appear to nullify their value. The heat of formation given for $[H_2O]$ is that resulting from the combination of *gaseous* oxygen and hydrogen, and as, in the cell, the oxygen is derived from solid lead peroxide and the hydrogen from liquid sulphuric acid, the figure is incorrect, being too high, although how much so it is impossible to say. But if the matter is followed up a little further it will be found that the heats of formation of both lead peroxide and sulphuric acid are also based on the assumption that their oxygen and hydrogen was originally in a gaseous state, and if, as happens here, they are not restored to the same state when these compounds are broken up, the negative heats of decomposition will be just as much too high as is the positive heat of formation of water, and so the errors cancel each other and do not vitiate the nett result.

The second objection is, in principle, of a very similar nature. Although the terms $[H_2SO_4]$ and $[PbSO_4]$ are necessary to a true representation of the reactions taking place, the heat of combination of neither hydrogen nor lead with sulphurion, SO_4 , is known, because the latter cannot be obtained in a free state. What the figures attached to these terms really represent is the heats of combination of hydrogen or lead, first with oxygen to produce water or lead oxide, and then with sulphur trioxide to form sulphuric acid or lead sulphate—that is $[H_2O, SO_3]$ and $[PbO, SO_3]$ —which is a very different matter. The mistake lies in having, for lack of knowledge of the heat of combination, $[O, SO_3]$, to treat sulphurion as if it were a mixture of oxygen and sulphur trioxide; but, however great may be the magnitude of this error, it appears equally in $[H_2SO_4]$ and $[PbSO_4]$; and as in the equation these are negative and positive quantities respectively, the two terms are mutually corrective.

Apart from the positive thermo-chemical evidence in favour of double sulphation, there is the further consideration that nothing approaching to an agreement between calculated and

observed E.M.F.s can be established on any other hypothesis. It is not worth while to give equations for all the various theories of the cell's reactions which have now been abandoned, and only the one alternative of single sulphation will be examined. According to this view the reactions taking place are as follows :—



and the corresponding thermo-chemical equation will be

$$\begin{array}{ccccccc} [\text{Pb}, \text{SO}_4] & - & [\text{H}_2, \text{SO}_4] & + & [\text{H}_2, \text{O}] & - & [\text{PbO}, \text{O}] = 79,650 \text{ cal.} \\ 112,970 & & 89,680 & & 68,360 & & 12,000 = 1.73 \text{ volts.} \end{array}$$

This gives the E.M.F. for an electrolyte of undiluted acid; for very dilute acid the E.M.F. is about 1.35 volts, and not more than about 1.4 volts for average working strengths, so it is very evident that the whole of the figures are hopelessly below what is required. Darrieus would provide part of the extra E.M.F. necessary to bring them into accord with observed results, on the supposition that the allotropic form of lead, of which he believes the negative active material to consist, is capable of generating a much higher E.M.F. than the ordinary metal, but it may be pointed out that, even were its combining energy raised to that of zinc, which is about what he claims, it would not nearly meet the case. FitzGerald adds an extra half volt to the equation by assuming that lead peroxide is an endothermic compound and liberates energy when it is broken up into a lower oxide and oxygen, but this does not seem to be in accord with accepted data.*

Temperature Changes during Discharge and Recharge.

In Ayrtton's investigations† of this matter he found that there was a sufficient development of heat during the recharge to raise the temperature of the cell nearly 1.5°C. above that of the surrounding air (see curve *a*, Fig. 158).

* FitzGerald appears to ascribe his negative figure to Thomsen, but the only determination of the heat of formation of lead peroxide given in Berthelot's "Electrochimie," published in 1897, is Tschelltzow's ([PbO, O] = +12,000 cal.), although he freely draws on Thomsen's data throughout the book. Nor can the writer find it in Thomsen's work itself, nor in Pattison Muir's book, which gives most of Thomsen's figures.

† *Journal Institution of Electrical Engineers*, Vol. XIX., p. 577.

The discharge followed immediately upon the recharge, and then the temperature at once began to fall again (*see curve b*). It is evident, however, that, even if the cell were left standing idle, it would gradually cool down to the level of its surroundings, so this curve by itself has no meaning, and the Author has added the dotted curve *d*, showing the rate at which the cell would cool under these conditions—that is, with no internal generation of heat taking place. By comparing these two curves it can at once be seen that an evolution of heat is going on throughout the whole of the discharge, but much smaller in amount than that of recharge. Some of this heat results from the ordinary C²R losses due to

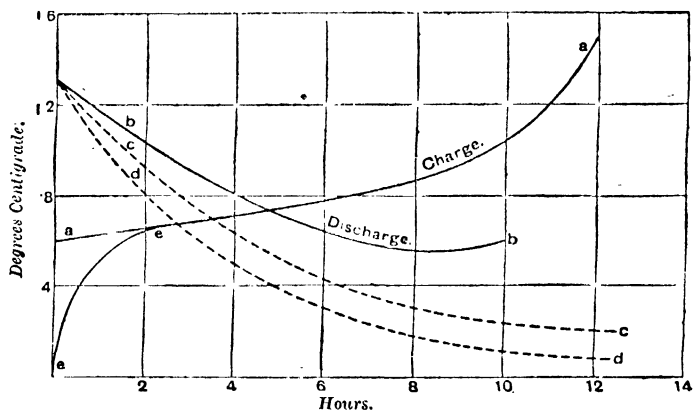


FIG. 158.—Curves of Temperature Changes on Discharge and Recharge.

the cell's internal resistance. Dotted curve *c* gives the approximate rate at which the temperature would fall if this were the only source of heat, and, on comparing the curve with curve *b*, it would appear that part of the heat of discharge arises from other causes.

For some inexplicable reason the cell did not always behave in the way just described, for at the end of some of the discharges its temperature was found to have fallen down to, or even slightly below, its surroundings; and this can have no other explanation except that an actual absorption of heat sometimes occurs on discharge. Unfortunately it so happened that in these instances the temperature was only read at the

beginning and end of the discharge, so it was impossible to construct a curve and see where this absorption of heat occurred or whether it was maintained throughout. The alteration in the rise of temperature on a recharge following a discharge of this nature is shown by curve *c*, which joins into the lower part of curve *a*; for beyond the point of junction the two curves were practically identical.

In Durcan and Wiegand's experiments* the discharge started with the cell at the same temperature as its surroundings, and they generally found that the temperature rose somewhat during the discharge. The heat evolved was, however, not always sufficient to cover even the internal resistance losses, and they concluded, therefore, that the discharge reactions must involve an absorption and direct conversion of heat into electricity. The observation that in certain cases the temperature fell slightly instead of rising afforded a direct proof of the correctness of their assumption.

This small cooling effect, which was detected independently in both researches, is in no wise mysterious or difficult to explain. It is, indeed, directly predicated, in accordance with Helmholtz's modification of Thomson's law, by the fact that the cell has a positive coefficient for its rate of change of E.M.F. with temperature; and it is quite unrelated to the necessity for restoring the heat of dilution to sulphuric acid when it enters into combination with the active materials, as that is fully allowed for in the E.M.F. of the cell and the thermo-chemical equations.

Although at times a good deal of stress has been laid upon the cooling effect on discharge, it may pretty safely be said that in practice it is more than masked by the dissipation of energy resulting from internal resistance and imperfect diffusion of the electrolyte, and that the nett result is seldom an absorption of heat, but rather its generation in small quantities.

The more important conclusion to be drawn from the temperature changes is the general efficiency of the discharge process in converting chemical energy into electrical energy, for such little heat as is produced may certainly be ascribed to the two causes just mentioned, and nothing is left over to

* *Electrical World*, Vol. XIII., p. 347, June 15, 1889.

support any theory such as that of the sulphation of the positive active material by local action. This could not possibly take place without the accompanying evolution of a very considerable amount of heat showing itself in a rapid rise of temperature throughout the discharge, but more especially at its commencement, when the acid in the pores of the active material is strongest.

The marked rise of temperature that occurs on recharge, as shown in curve *a*, Fig. 158, proves this process not to be so efficient as that of discharge. The same fact is borne out in every day practice by the high voltage required to effect a recharge; a P.D. commencing not much below 2.2 volts and rising to 2.5 volts or more being necessary to reverse a set of reactions which can only yield about 2 volts on discharge. A small portion of this loss is of course due to internal resistance and liquid polarisation, *i.e.*, imperfect diffusion effects; but the remainder must be directly ascribed to the gaseous polarisation of the electrodes. To further explain this statement, it has to be remembered that the primary reaction of recharge—the one which can commence with the least expenditure of E.M.F.—is the liberation of oxygen and hydrogen. These gases rapidly concentrate at the electrodes until the impressed E.M.F. exceeds 2 volts, and only then can the desulphation of the active materials begin, accompanied by a very slight escape of gas. When this stage is completed, the reaction returns to a further liberation of oxygen and hydrogen, the gas pressure again rises, and they pass off in large quantities at an E.M.F. of 2.5 volts and upwards. The whole recharge, in fact, takes place through the agency of gaseous polarisation, and under these conditions it is fundamentally impossible for electrical energy to be converted into chemical energy without a considerable percentage being dissipated as heat at the same time.

CHAPTER VI.

THE DESIGN OF LEAD CELLS.

From a purely electrical standpoint the best lead cells are those which enable the fundamental requirements of their active material—i.e., free diffusion of acid into it from the electrolyte; free conduction of current from it to the external circuit—to be most perfectly fulfilled; and in which the design and disposition of the supports are such as will allow the most uniform distribution of the work throughout all parts of the active material when the electrodes are opposed to each other in the cell. It needs but little consideration to see that these conditions cannot be better fulfilled than by the simplest arrangement; merely plates of lead covered with an exceedingly thin layer of active material and set at a uniform distance apart; the very lines indeed on which Planté's original accumulators were constructed, sometimes with the electrodes wrapped together spirally, sometimes with flat plates parallel to one another, as still remains the general practice.

Commercially speaking, however, the art of designing storage cells and their electrodes consists in effecting the best possible compromise between the above conditions, which are those favourable to efficiency and durability, or, in other words, to low working and maintenance expenses, and those conditions which tend to a reduction of weight, space and prime cost; an altogether different and more difficult problem.

Something similar might doubtless be said of most articles of purely utilitarian value, but the trouble in this instance is that the position of the storage battery as a practical

electrical appliance is so entirely dependent on the degree to which the conflicting requirements can be reconciled, while the margin to spare between them appears to be almost used up. Its present footing is, in some directions, a rather precarious one; a nice balance of pros and cons which may not always work out so favourably and might lead to a partial replacement of the battery by generating machinery; but, on the other hand, could the storage battery only be rendered some 20 to 50 per cent. more durable or less weighty and costly than it now is, it would certainly achieve an enormously extended application in more directions than one.

Treatment can in itself altogether determine the life of any make of electrode, from the best to the worst, and as no two batteries, however well looked after, are ever served quite alike, it is impossible to set up any very rigid standard of permissible depreciation; but for stationary batteries of fair size the rate of maintenance for periods up to ten years generally range from 5 to 10 per cent. of the selling price, although it is certain that the manufacturer must sometimes incur loss at the lower figure. The cost of maintaining a battery is practically that of renewing the plates, and these rates roughly correspond to an assumed life of three to six years for the positives and five to ten years for the negatives. "Life" in this connection does not mean until the positives break down mechanically or the output of the battery becomes a negligible quantity, but is always limited to the period during which a definite and reasonable percentage of the initial output can be obtained. Sometimes the full specified output has to be maintained, but more usually a decrease of 20 to 40 per cent. is allowed.

The relative importance of the two factors in the compromise between prime cost and depreciation varies with circumstances, and in special cases, such as cells for use in automobiles, both may have to give way before considerations of weight and bulk; but in an ordinary way the above-mentioned requirements must be complied with, and have to be borne in mind at all stages of designing. More expensive batteries of greater durability will not sell because the purchaser is sceptical; and cheaper batteries with a shorter life are soon found to be more costly in the end.

It is now apparent why flat sheet electrodes were only the first word in battery construction, for, assuming that the plates are thick enough to withstand a fair amount of peroxidisation without undergoing disintegration or distortion, and that their covering of active material is thin enough to remain securely in position without further support, the amount of lead necessary for a given output is so great as to render their cost excessive and their weight and bulk prohibitive. The next step, therefore, was to increase the thickness of the layer of active material, while keeping the lead sheet as before, and this is what Faure did when he discovered how to prepare active material from lead oxides; but the adhesion of the thicker layer to the plate was insufficient to retain it in its place, and independent support had to be provided. Finally, this method also proving unsatisfactory, the support itself was modified by devices due to Swan, Sellon, Phillipart, Brush and others, so as to relieve the contact surface from the strain due to the weight of the active material or other incidental forces, and thus the cellular and grooved electrodes were evolved.

Further difficulties, however, yet remained to be faced. It was found that the positive grids and supports were rapidly peroxidised and destroyed by local action, and that the active material they contained soon underwent an increase of bulk, which either brought about its disintegration or caused it to break away from the support, or else the support was itself buckled or ruptured. At the other electrode no such phenomena were observed, and for this reason the design of the positive so as to prevent its rapid deterioration monopolised attention for some years, and the poor negative came to be regarded as little more than an incidental adjunct to the cell: a point of view from which it is still occasionally regarded. Every other consideration was ignored in the futile and misdirected endeavour either to abolish the positive support altogether or else to make it so strong and rigid and of such a construction that it could forcibly detain the active material and prevent its expansion. Those were the dark days of the storage battery, when the first uncritical enthusiasm over its introduction had died away and it seemed likely to prove incapable of satisfying even the very moderate demands of

the engineering practice of that period. Gradually, however, things took a turn for the better. The first great step was to put the methods of treatment upon a proper basis ; next, the imperative necessity for purity in the materials used in the cells and for a closer attention generally to the details of construction also began to be better realised ; and then came a return to supports of large surface and active materials in thin layers, but now embodied in electrodes of more practical design and improved manufacture. The change was initiated with formed plates, but the pasted electrodes were in some cases also modified to comply with the same conditions.

Active Materials.

As the generation of electricity by the cell is the result of chemical reactions proceeding between the active materials and the electrolyte, any portion of the active materials not in direct contact with the electrolyte is useless ; so not only must they be porous but this porosity must be thoroughly molecular. That is to say, in addition to the spaces of appreciable size that exist between the small visible particles, each of these particles must itself be chemically permeable in order to include every molecule in the electrolytic circuit. Active materials as ordinarily prepared from metallic lead or lead oxides necessarily fulfil this condition, for if the electrolyte had not had access to the individual molecules, their complete conversion into spongy lead and lead peroxide would not have been possible ; and, presumably, each molecule is left surrounded by a space, also of molecular proportions, which the elements in combination with it, either before or during the formation, had previously occupied. But although the pores and spaces are there they are quite inadequate to contain anything like the quantity of sulphuric acid that is needed for the full discharge of the adjacent active material. Solid lead requires about eight times, or solid peroxide about six times, its own volume of a solution of sulphuric acid, specific gravity 1·200, for its 50 per cent. sulphation, even if the whole of the acid were abstracted in the process ; while, to still leave an electrolyte of reasonable strength at the end of the discharge, double these quantities would be necessary.

On the other hand, one may safely say that it has not yet been found possible to prepare a practical active material which could contain more electrolyte than corresponded to two-thirds its apparent volume, or a peroxide material which held more than half its nominal bulk; that is, two volumes of electrolyte to one volume of solid lead, and one volume of electrolyte to one volume of solid peroxide. Half the above proportions, or one volume of electrolyte to one of lead or two of peroxide, is a more average ratio, for in many cases the porosity must be very much less.

These figures show very clearly that it would be quite impossible for the active materials to properly fulfil their functions unless the depleted solution in their pores were continually replenished by a transference of acid from the main body of the electrolyte, and this necessity for diffusion constitutes one of the fundamental weaknesses of lead cells. The way in which it reacts unfavourably upon the output, efficiency, and almost every other property of the cell, just in proportion to the extent to which it has to take place and the degree in which it is impeded, has already been discussed at some length in Chapter IV. and need only be referred to here to emphasise the importance of great porosity in the active materials. The same conclusion can now be reinforced by another consideration.

Both the positive and negative active materials are popularly supposed to expand during discharge and contract during recharge in the sense that they undergo an alternate increase and decrease of superficial volume which may be likened to the swell and subsidence of the chest in the act of breathing. It is difficult to understand why this idea receives such general credence, for it has to face the apparently fatal objection that lead being without elasticity, the support could not follow the contraction of the active material, even if it yielded before the expansion, and so in a very short time the contact between the two would inevitably be severed; in fact, the lead accumulator would become a sheer impossibility. The true explanation of what happens appears to be that, although spongy lead and lead peroxide do increase in bulk when they are sulphated in the course of the discharge, yet under normal conditions the whole of this growth is taken up

internally, without their external boundaries undergoing any change, and so the contact with the support remains unaffected. That is to say, the porosity decreases on discharge, but the action being a perfectly reversible one, it is restored to its original value on recharge.

But if the porosity is too limited, or from over-discharge or other causes the active material becomes excessively sulphated, the space within the pores may prove insufficient to meet the demands made upon it. In the case of the hard incompressible lead peroxide the entire volume of the part affected must then expand, and in so doing either break away from the support, stretch, buckle or burst the support, or be itself broken up, according to the nature of the electrode. All these effects are familiar occurrences in positive plates. It has already been mentioned that at one time they threatened the ruin of the storage cell altogether, and even now crop up as a result of bad construction or treatment, on far too slight a provocation; but as a large number of batteries go on for years without showing any signs of them, their appearance must be regarded as too occasional to be the result of any normal and constantly repeated action.

The spongy lead of the negative electrode is almost always more porous than the peroxide active material, so better provision exists for internal growth on discharge and sulphation. Besides, it is too soft and yielding to be capable of putting any considerable strain upon its support or of disintegrating itself easily, and it is not surprising therefore to find that the expansion effects of the positive are never reproduced to any marked extent.

So much for the active material's relations to the electrolyte. Electricity having been generated in virtue of their characteristic chemical properties, it is next conveyed to the support by reason of their inherent conductivity. The specific resistance of solid lead is rather more than thirteen times that of copper. The specific resistance of solid lead peroxide is not known, but, according to data furnished by Shields,* its powder, dried at 100°C. and held together by compression, has a resistance about six times that of sulphuric acid diluted to its

* *Chemical News*, Vol. LXV, p. 87.

stage of greatest conductivity. In all probability, however, the resistance of lead peroxide under the conditions which it presents as the active material of a positive electrode—hydrated and bound together by a natural cohesion—is far below this figure, for otherwise it could not exhibit such remarkable powers as a depolarising agent; but, on the other hand, it is not likely that it ever approaches anywhere near to that of the uncombined metal.

Whatever the specific resistances of lead and lead peroxide, considered as solids, their resistances per unit volume of the porous materials will be very much greater; while it is also evident that their actual amounts will vary and increase in some sort of direct ratio with the porosity. The two essential qualities of an active material, conductivity and porosity, are therefore in direct conflict, and neither can be pushed to an extreme at the expense of the other. On the one hand, practically solid materials, such as may be obtained by subjecting spongy lead to great pressure or by depositing peroxide, under certain conditions, from an alkaline solution of litharge, are of no use; on the other hand, active material in powder or lumps packed loosely together after the manner of the manganese dioxide of a Leclanché cell is equally valueless. All the same, it is possible to conceive an active material of extremely high porosity and yet containing a sufficiency of conduction and coherence, because the quality of the porosity has also to be taken into account as well as its mere amount or total volume of spaces in a unit volume of material. By “quality” is meant the relative size and distribution of the spaces; and the more thoroughly these can be reduced to molecular proportions and distributed uniformly throughout the mass the greater will be the permissible limit of total porosity.

Mechanical strength is a property rightly to be desired, although in itself it does not guarantee durability, but rather the reverse if it arises, as is often the case, from insufficient porosity; for then the active material, not having room to expand internally when sulphating, especially if any abnormal sulphation takes place, soon racks itself to pieces. For instance, reduced lead prepared from litharge which has been cast when in a molten state, is almost as dense and tough as the solid metal, but it begins to scale and break up after a

few discharges. Conversely, a material that, owing to its high porosity, is weak mechanically, might last extremely well, as ample room would be provided for alterations of volume due to changes of chemical composition, and all molecular stresses would thereby be eliminated. A distinction must also be made between strength and coherence. The former implies the latter, but the latter does not necessarily include the former. A negative active material may be exceedingly soft and yielding, and a positive material may be fragile and brittle, yet, except under the influence of strains they are not intended to endure, each may exhibit an excellent coherence; and this is the more essential quality, for it implies conductivity.

The coherence, conductivity, porosity and other properties of an active material are largely decided by the methods of its manufacture, and, as a rule, cannot be designedly varied beyond small limits without a great change of procedure. In most cases it is difficult or impossible to directly measure them, and they have to be judged as a whole on the strength of the results that can be obtained from the electrodes of which it forms a part. This plan has the disadvantage that it is often difficult to know precisely where praise or blame should be assigned or in which direction improvements should be effected. Well-proportioned supports may be discredited by bad active material, and good material sometimes achieves a transitory success for supports of radically wrong construction; but in any event it is most important to obtain a high specific output from the active material, not only because it is a valuable property in itself, and enables weight and cost to be reduced, but because it indicates the existence of a state of affairs which conduces to durability. An active material, which, by reason of its own nature, its method of mounting in the electrode, or its conditions of treatment, only yields a low specific output, is almost certain to depreciate rapidly.

In practice, no fixed relationship exists between quantity of active material and its output. The nearest approach to one occurs in the case of Planté-formed electrodes, whose thin layers of active material have large surfaces of contact with the support on the one side and the free electrolyte on the other; and then, if the discharge be slow, say, not exceeding a

nine-hour rate, a direct proportionality may be assumed, although it cannot easily be verified on account of the difficulty of determining the amount of active material present. In all other cases, the output per unit of active material is more or less dependent upon every detail connected with its manufacture, its manner of mounting in the support, and the treatment to which it is subjected. To mention only the principal causes of modification, the output varies inversely as the rate of discharge, the density and thickness (measured at right angles to the surface of contact with the free electrolyte) of the active material, and its amount per unit area of support contact.

Each of these variables is so intimately bound up with and dependent upon the others that it is extremely difficult to disentangle and discuss them individually. The density or porosity of the active materials being a factor about which very little is definitely known either as regards its value or its effects, there is generally no alternative but to provisionally treat them as if they were all alike in this respect, although such is far from being the case, and, by so doing, much misunderstanding as to the real source of the large differences of output between one make of cell and another is often caused.

The effect of the thickness of an active material upon its output is closely related to the density of the active material, nor can it be considered apart from the rate of discharge. The faster the discharge the more nearly is the total output confined to those layers in immediate contact with the free electrolyte; the slower the discharge, the deeper is the strata from which a useful contribution can be exacted. On excessive discharges, amounting almost to a short circuit, the output becomes a mere skimming of the surface of the active material, while on abnormally slow discharges, spread over days and weeks, almost any depth may ultimately be tapped. Generally speaking, therefore, the thinner the active material the larger will be the output per unit weight; and experience has shown that with an average quality of material and medium rates of discharge, it falls off very rapidly for thicknesses exceeding about $\frac{1}{4}$ in.

It follows as the converse of what has just been said that the relationship between rate of discharge and output depends

in its turn upon the thickness of the active material; and, in addition, it is largely determined by the area of support contact. In the best commercial types of cells the output obtainable at a nine to twelve-hour rate is diminished by about 25 per cent. at a three-hour rate and by about 50 per cent. at a one-hour rate; but in many cases, especially if Faure type electrodes are used, the falling off is somewhat greater; and if the active material is thick and its coefficient of support contact low, there is no limit to the reduction of specific output that may occur.

It has long been known to everyone having any practical experience of lead cells that their output, and many other of their properties, are largely influenced by the ratio between the amount of active material and its area of contact with the support, or, as it will here be termed, the coefficient of support contact; but the knowledge has never been very definitely formulated. A recognition of the importance of this factor receives crude expression in the figures which are so frequently given of the proportion existing between the weight of active material and either the weight of the support or the total weight of the electrode, but the matter is then obscured by other quite unrelated variables depending upon the nature of the support itself. This point and others connected with the conditions which control the specific output of the active material when in the electrode are more fully considered on p. 265 *et seq.*, and figures are given for the outputs actually obtainable.

Supports.

So far, the qualities requisite in the supports have not been considered, except indirectly, with regard to the area of contact surface they provide for the active material. Besides this, their electrical conductivity must be taken into account, and also, in many cases, their mechanical strength and rigidity. The support being the path by which the current passes to and from the external circuit, it must be of sufficient cross-sectional area, else its resistance will bring about too great a fall of potential between one part of the electrode and another, and cause the chemical changes in the active materials to proceed at such different rates that those portions

nearest to the connecting lug will be overworked before those furthest from it have done their normal amount. The larger, therefore, the rate of output per unit of support surface the greater must be the weight of metal behind that surface, or, in other words, the thicker must it be. With formed supports the rate of output per unit of surface is necessarily so limited, in spite of the heavy discharges often taken from them, that very thin metal may be employed; but with Faure type electrodes, where the area of support contact per unit of active material is generally far less, a stouter support becomes necessary even for slow rates of discharge.

In the case of positive supports an additional factor comes into play which sets a definite limit to their permissible thinness, and that is their rate of disintegration under the slow but continual oxidation by local action. If the electrodes are of the Planté type, the attack is purposely accelerated during the formation process, and it is easy to make a rough calculation which shows that a layer of active material yielding 6 ampere-hours per 100 sq. in. of support contact (the output of an average formation) requires the peroxidisation of a skin of metal about $\frac{1}{400}$ in. in thickness. As both sides of the metal are affected, making $\frac{1}{200}$ in. in all, and the corrosion is sure to penetrate deeper in some places than in others, it may be approximately assumed that the formation breaks up solid metal $\frac{1}{100}$ in. in thickness, and experience confirms this view, for it is of little use introducing lead thinner than 0.01 in. or 0.25 mm. into an electrode to be formed unless its early and entire conversion into active material is desired. The endurance and life of the supports rapidly increases with metal of greater thicknesses, because, once a good dense coating of peroxide of a certain depth is produced, it almost cuts off the lead underneath from contact with the electrolyte, and further local action then proceeds extremely slowly, provided no dangerous impurities are left over from the formation or are introduced into the cell afterwards, and that the lead itself was initially pure, dense and homogeneous. If these conditions are not fulfilled, supports of almost any thickness may be quickly oxidised through and through; but otherwise it is found that metal $\frac{1}{32}$ in. to $\frac{1}{16}$ in. or 0.75 mm. to 1.5 mm. thick will last for a considerable number of years.

The simplest way of conveying some idea as to the durability of positive supports is to state the thickness of the ribs, strips, or other subdivisions of which the bulk of the support is constituted. Another method often adopted is to give their surface per unit of weight, and the table on p. 270 contains some approximate figures for this ratio per pound and per kilo of sheet lead; but they equally apply to the metal whether used as strip or tape, or whether it assumes the form of ribs or other portions of a cast support.

A favourite plan with makers and inventors is to state the ratio between the actual and nominal surface of the support, when of the Planté-formed type. In examining such figures care should be taken to ascertain what is meant by "nominal surface," whether it refers to the surface of one side only—the "linear area" or the "projected area" of the plate, as it is variously termed—or whether it includes both sides. The former is sometimes made the standard of reference because it doubles the ratio and furnishes the more imposing figure, but, as both sides of the electrode count in the cell—excepting end plates—the latter is certainly the correct one to employ. Even then the ratio conveys no very definite or useful information unless accompanied by other data, for it does not indicate how far durability has been studied, or if the lamination has been carried to excess in an endeavour to obtain a large output for weight. Of two plates of similar design and possessing an equal ratio of actual to nominal surface, but one twice the thickness of the other, the latter would in reality be twice as finely subdivided. Besides this, the ratio also varies with the width of the grooves or spacing between the ribs or other component parts.

Well-designed supports can be cast with an actual surface eight to ten times their nominal surface; but if a still greater ratio is desired other methods of construction must be substituted.

Electrodes.

On passing to a consideration of the behaviour of active material and support when in combination, it will be found that, assuming equal qualities of active material and similar conditions of treatment, the actual and comparative merits of

electrodes are chiefly determined by the area of their support surface relatively to the quantity of active material, and the position of their support surface relatively to the active material and the free electrolyte.

The relative amount of support surface is, indeed, the keystone of electrode design, for not only does this in itself largely determine the relative positions of the support and the active material, but it is also one of the chief factors which control the specific output of the active material, and through that, as already stated, the durability.

In Planté-formed electrodes the proportion of support surface is necessarily large, because the nature of formation processes is such that it is extremely difficult to attack the support to any considerable depth without a part or the whole of the peroxide being loosened and falling away, and consequently a thick layer of active material cannot be obtained. As, however, neither the weight nor volume of the active material is directly ascertainable, their relation to the support surface can only be arrived at through the output per unit of support surface. This ratio never varies between very wide limits. A well-formed plate will yield about 1 ampere-hour for every 100 sq. cm. or per square decimetre, of support surface, or about 6 ampere-hours per 100 sq. in. A specific output of half these values—that is, 0.5 ampere-hour per 100 sq. cm., or 3 ampere-hours per 100 sq. in.—is the least that would be of much practical use; indeed, supports will form up to this extent by local action in the course of twelve months' ordinary usage. A specific output of double the values—*i.e.*, 2 ampere-hours per 100 sq. cm., or 12 ampere-hours per 100 sq. in.—represents about the extreme limit to which a formation can ordinarily be pushed. Even that means a thicker coating of peroxide than can be relied on to maintain itself in contact with the support by cohesion merely, and it is only feasible in such positions as narrow grooves or spaces where the adjacent layers can meet together and pack and wedge themselves securely in their place. Such a state of affairs is not to be recommended, as, by considerably reducing the surface of contact between the active material and the free electrolyte, and prematurely filling up space which should be left available for future

growth, it necessitates the sacrifice of some of the special advantages which pertain to the use of formed electrodes. The first of the figures just given may be regarded as corresponding to an average formation; any coming below or above it to light or heavy formations.

It is not easy to construct practical Faure type electrodes with as small an output per unit of support surface as formed plates, and about 12 ampere-hours per 100 sq. in. is the upper limit of the one and the lower limit of the other; but the proportion of applied active material can be increased almost indefinitely so far as structural difficulties are concerned, and although the output does not go up in the same proportion, because the specific output of the active material undergoes a simultaneous decrease, yet it may in certain cases reach to hundreds of ampere-hours per 100 sq. in. of surface. When the amount of active material that any support will contain can be ascertained by direct experiment, or be approximately calculated, its area of contact with the support can be expressed in terms of unit weight; but in designing electrodes, volume of active material, or rather the volume of the space in and around the support which it is proposed to fill with active material, is often the more useful standard.

The weight of active material that will go into a given space varies considerably with its mode of manufacture and the raw material from which it is produced. If it is the most usual kind, prepared from a paste of litharge or red lead, 3oz. per cubic inch or 5 grammes per cubic centimetre is about the average figure for an active material of ordinary coherence and porosity. Should the paste be very loosely applied to the electrode, or mixed with other substances which are dissolved out during formation, it may not yield above 2oz. of active material per cubic inch, while if it is compressed 4oz. may be put into a cubic inch, or even considerably more should the pressure be great and the oxide but coarsely powdered. In such cases, however, there is a large sacrifice of porosity.

The following table shows the extent of the surface in contact with the support per unit volume of active material for plain sheet supports, grids with square holes, and strip or

slotted supports. In the two latter cases the ratio is independent of the thickness of the active material; in the former case it is inversely proportional to its thickness. The figures for the grids and slotted plates are based on the assumption that the active material does not cover or project beyond the edges of the supports but finishes off flush with them:—

Table of the Area of Support Contact per Unit Volume of Active Material in Sheet, Grid, and Slotted Supports.

Support surface per cubic inch or cubic cm. of active material.		Sheet supports. Thickness of active material on either side.		Grid supports. Length of side of square pellets.		Slotted supports. Width of slots.	
Sq. ins.	Sq. cms.	Inch.	Mms.	Inch.	Mms.	Inch.	Mms.
32	...	$\frac{1}{32}$...	$\frac{1}{8}$...	$\frac{1}{16}$...
...	10	...	1	...	4	...	2
16	...	$\frac{1}{16}$...	$\frac{1}{4}$...	$\frac{1}{8}$...
...	6·7	...	1·5	...	6	...	3
...	5	...	2	...	8	...	4
10·7	...	$\frac{3}{32}$...	$\frac{3}{8}$...	$\frac{3}{16}$...
...	4	...	2·5	...	10	...	5
...	3·3	...	3	...	12	...	6
8	...	$\frac{1}{8}$...	$\frac{1}{2}$...	$\frac{1}{4}$...
6·4	...	$\frac{3}{32}$...	$\frac{3}{8}$...	$\frac{3}{16}$...
...	2·5	...	4	...	16	...	8
5·3	...	$\frac{3}{16}$...	$\frac{1}{4}$...	$\frac{3}{8}$...
...	2	...	5	...	20	...	10
4·6	...	$\frac{7}{32}$...	$\frac{7}{8}$...	$\frac{7}{16}$...
...	1·7	...	6	...	24	...	12
4	...	$\frac{1}{4}$...	1	...	$\frac{1}{2}$...

Electrodes having coefficients of support contact exactly similar to those given above will probably not be encountered in practice, because the simple forms there dealt with are generally modified by perforations in the sheets, sloping walls to the grid bars, oblong instead of square apertures, central webs to the slotted supports converting them into grooved plates, and so forth, but they will serve as standards with which all the different designs can be compared.

The coefficient of support contact for most Faure type plates will be found to fall within the margins of the table. Electrodes consisting of a wire buried in a large mass of

active material, or a simple frame surrounding a big slab, may, no doubt, possess much lower coefficients than are included in its scope, but they are the exceptions.

Theoretically it should be possible to construct a curve showing the specific output corresponding to any given ratio between the amount of active material and the area of support surface; but the matter is so complicated with other variables that one has to be content with a much vaguer and more general idea of their relationship.

In round numbers, the practical maximum of output for weight of applied active material is 110 ampere-hours per kilo, 50 per pound and 3 per ounce, or half these outputs if the total quantity of active material at both positive and negative is to be taken into account. It is probable that these large outputs are generally attained, and even exceeded, by the active material of Planté-formed plates, but they can seldom be permanently realised from pasted electrodes. They require very porous active materials, having a large contact surface with the support and the free electrolyte; that is to say, thin electrodes, well-distributed and subdivided supports, low discharge rates, and the best treatment generally—in fact, a combination of all the most favourable conditions. A departure from any one of these will mean a proportionate reduction in the specific output. In ordinary continuous commercial usage, about two-thirds of the above values, or 65 to 75 ampere-hours per kilo, 30 to 35 per pound, and 2 per ounce, is as much as can be expected, and even then only if there are at least 8 sq. in. of support-surface per cubic inch of active material. Not that this arbitrary figure represents any real limit, or that the specific outputs will be uniform within its bounds. It is merely a result which can be reached in practice with some difficulty, and beyond which the decrease of specific output seems to become more noticeable.

When the support surface is reduced below 8 sq. in. per cubic inch of active material by using the latter in thicker layers, there is, as already stated, such a rapid falling-off in specific output, due to the greater distance of the free electrolyte from its innermost portions, that it is worse than useless to do so unless the porosity of the active material is exceptionally

great or the rate of discharge exceedingly low. When the proportion of active material is increased by additions in some direction other than thickness—such as by using a grid with larger apertures—the decrease of specific output is so much more gradual that no very precise limit can be fixed beyond which it is inexpedient to go.

Taking the above figures in conjunction with those previously given for the relation of weight to volume, the average output for volume of active material works out at 6 ampere-hours per cubic inch and 0.33 ampere-hour per cubic centimetre; or, if the maximum output is required, 9 ampere-hours per cubic inch and 0.5 ampere-hour per cubic centimetre.

Output for Weight of Electrode.

The output per unit of surface of a Planté-formed electrode being known, its output per unit of weight can be ascertained if its surface per unit of weight is known also; and these two ratios are given for lead of various thicknesses in the following table. It will, of course, be understood that the thickness here considered is not that of the electrode as a whole, but of the ribs or other parts of which it chiefly consists. The outputs are calculated on the basis of 6 ampere-hours per 100 sq. in. and 1 ampere-hour per 100 sq. cm. of surface, as this is the average and most usual proportion. If it is found that the formation process used yields rather higher or lower results, the outputs can easily be re-computed to suit them, but they are never likely to be more than twice or less than half the value of the figures given.

It may be noticed that the outputs per pound and per kilo do not bear quite the correct relation to each other. This is because the two standards adopted—and which are purely approximations—have been adjusted to the nearest whole numbers, in order to render them more easy of practical application. Strictly speaking, the output per 100 sq. cm. should be taken as 0.923 ampere-hour, but the figures in the decimal places are really quite meaningless.

The table takes no account of edge surface. Should there be any it can readily be estimated, or it may be neglected and offset against the loss of surface in strengthening ribs of

stouter metal than the others. The figures are also independent of the connecting lug, surrounding frame, central core or any such parts which contribute practically nothing to the surface or output, but add very considerably to the weight. To arrive at the total weight of an electrode of any desired size and type, they should be separately determined at the rate of 0.4lb. or 6.5oz. of solid lead to the cubic inch, and added on.

*Table of Surface Area for Weight of Sheet Lead.
Also of Output for Weight when formed.*

Thickness of lead in inches.	Approx. thickness in mm.	Sq. in. of surface per lb.	Sq. cm. of surface per lb.	Sq. cm. of surface per kilo.	Ampere- hours per lb.	Ampere- hours per kilo.
$\frac{1}{8}$	3.1	40	256	560	2.4	5.6
$\frac{1}{16}$	2.5	50	320	700	3.0	7.0
$\frac{2}{32}$	2.0	63	400	880	3.8	8.8
$\frac{1}{16}$	1.55	80	510	1,120	4.8	11.2
$\frac{1}{32}$	1.25	100	640	1,400	6.0	14.0
$\frac{1}{64}$	1.00	125	800	1,760	7.5	17.6
$\frac{1}{128}$	0.85	150	960	2,110	9.0	21.1
$\frac{1}{256}$	0.62	200	1,280	2,815	12.0	28.1
$\frac{1}{512}$	0.50	250	1,600	3,520	15.0	35.2
$\frac{1}{1024}$	0.42	300	1,920	4,225	18.0	42.2
$\frac{1}{2048}$	0.36	350	2,240	4,930	21.0	49.3
$\frac{1}{4096}$	0.31	400	2,560	5,630	24.0	56.3
$\frac{1}{8192}$	0.28	450	2,880	6,335	27.0	63.4
$\frac{1}{16384}$	0.25	500	3,200	7,040	30.0	70.4

The highest figures included in the table cover the maximum surface and output for weight of complete electrode which can at present be attained, but in most cases results which fall very considerably short of them have to suffice. For one thing, it has not yet been found possible to cast supports in which the ribs average less than about $\frac{1}{30}$ in. in thickness, and to do even this requires skill and experience; but if, by the use of special methods, the lamination of the metal is carried much further, or if lead sheet, tape or wire is prepared of any required thinness by rolling or squirting, and is then made up into electrodes, its subdivision is restricted by the fear of the supports breaking up during formation, or the certainty of the positives doing so by local action too soon afterwards. For the same reason

the alternative method of increasing output by deeper formation and thicker layers of active material is not applicable to supports of very large surface area for weight, and in any event it very much diminishes the excellence of the electrode.

It is not often possible, and if possible not wise, to make the ribs or other divisions of a positive support less than about $\frac{1}{32}$ in. or 1mm. in thickness; to provide less space between them than is equivalent to grooves $\frac{1}{32}$ in. wide; and to allow more than $\frac{1}{2}$ in. (exclusive of the solid central core should there be one) from face to face of the electrode. The nett result of all these limitations is that the output per weight of Planté-formed positive electrodes capable of undertaking the average work of stationary cells without their depreciation exceeding the ordinarily accepted standard is seldom more than 6 to 9 ampere-hours per pound at slow rates. Formed negatives frequently yield rather higher results because the quantity of active material relatively to the support can be somewhat increased with safety.

The output per unit of weight or volume of an electrode containing applied active material is most conveniently expressed with reference to the proportions existing between the quantity of active material and the support; and some data arranged in this way are given in the table below. They presume that the active material furnishes 30 to 32 ampere-hours per pound, or about 65 ampere hours per kilo, and weighs 3.25oz. per cubic inch. The reason for adopting the latter precise figure is that, besides being close to the average, it represents just half the weight of a

Table of Specific Outputs of Pasted Electrodes.

Ratio of active material to support.		Ampere-hour output of electrode.			
By weight.	By volume.	Per lb.	Per kilo.	Per cub. in.	Per cub. cm.
1 : 4	1 : 2	6.0	13	2.0	0.110
1 : 2	1 : 1	10.0	22	3.0	0.165
1 : 1	2 : 1	15.0	33	4.0	0.220
$1\frac{1}{2}$: 1	3 : 1	18.0	40	4.5	0.250
2 : 1	4 : 1	20.0	44	4.8	0.265
$2\frac{1}{2}$: 1	5 : 1	21.0	47	5.0	0.277
3 : 1	6 : 1	22.0	50	5.3	0.286
4 : 1	8 : 1	23.5	52	5.4	0.300

cubic inch of solid lead, 6.5oz.; and it thus enables the simple ratio of 1 : 2 to be established between the relations of the active material to the support by weight and by volume respectively.

Although the table is based on the assumption that the specific output of the active material is unaltered throughout, it follows from what has previously been said that this can only be expected to hold good if the coefficient of support surface also remains uniform; that is to say, as the proportion of active material is increased, the subdivision of the metal in the support must also go up in a like degree. In the opposite and more likely event of the same minimum stoutness of support being supposed or used, whatever the quantity of active material, then the higher figures in the table will not be realised because of the diminution in the specific output of the active material. In practice it is not easy to construct a durable electrode with a support of sufficient conductivity and a coefficient of support surface high enough to ensure a good specific output from the active material without the weight of the support is at least equal to that of the active material. The ratio between them is generally something from 2 : 1 to 1 : 1, with the accompanying outputs of 10 to 15 ampere-hours per pound of complete electrode.

Relative Output of Positives and Negatives.

So far the relations and proportions to be observed between active material and its support have been treated as if they were identical for both positive and negative electrodes, but this is not entirely so by reason of the differences in the qualities of the two active materials. Of spongy lead and lead peroxide prepared by the same processes and from similar materials the latter must inevitably possess less porosity and conductivity than the former, and, provided both are either formed or pasted, this will hold good even with considerable differences of manufacture. The consequence is that the maximum permissible distance of any part of the active material from its support or the free electrolyte is less in the case of the peroxide; while, owing to its liability to expansion troubles on the slightest provocation, the minimum specific

output at which it can be satisfactorily worked is higher than that for spongy lead.

It does not follow, however, that positives and negatives should not be of like design, for if it is one which fulfils the former's more exacting requirements, this simply means that the latter is well on the right side; and the point must really be decided by the relative outputs it is desired for them to possess.

There is no fixed rule as to whether the positives and negatives in a cell should be capable of furnishing equal outputs, or which should preponderate over the other; any one of these alternatives may be preferable according to the nature of the electrodes and the circumstances of their use.

If the positives have a small coefficient of support contact and are liable to be exposed to adverse treatment which will readily bring about their abnormal sulphation, their output should be the greater, so that by the running down of the negatives they are automatically protected from over-discharge, and can also afford to lose some proportion of their active material without diminishing the output of the cell. But if the positives have a large support surface and are fairly well looked after, the slow peroxidation of their metallic lead by local action may compensate for loss in other ways, and it will then be the negatives where the excess of output should be provided, for, although they do not readily shed their active material, their output in the course of time almost invariably decreases from not very well understood causes. For a state of affairs somewhat intermediate between these extreme cases, and where the falling-off in output goes on at about the same rate at both electrodes, initially equal outputs would be the most appropriate.

If positives and negatives of similar size and construction are used together, the latter will possess the larger total output because of the greater specific output of their active material. If it is wished to make it equal to or less than that of the positives, the quantity of active material must be reduced, and this is most conveniently done by making the electrodes thinner. In cells with pasted electrodes it is very usual to see negatives combined with positives quite half as thick again, but this does not prove that they have the lesser

output, for if the rates of discharge are high quite 50 per cent. more peroxide may be required to make up for its lower specific output.

At one time positives were almost invariably so proportioned that their output was equal to or somewhat greater than that of the negatives, but since heavier and more durable designs have been adopted, this plan is chiefly confined to cells for traction or other special purposes; and in stationary batteries the negatives generally have a very considerable surplus of active material and output. In fact, any other course is hardly possible with batteries worked under low maintenance rates based on the assumption that the negatives will last out two sets of positives without their output falling below the specification limit. A very usual plan is to employ Planté-formed positives, but negatives containing applied active material. This ensures the most favourable conditions for overcoming the inferior porosity and conductivity of the peroxide, and at the same time presents no difficulties to the construction of negatives of very much the larger capacity. In many respects it would be advantageous to use formed negatives also, but it is then almost impossible to get so large a surplus output, and in any case their manufacture is more troublesome and expensive.

Design of Electrodes.

It will be evident from all that has previously been said regarding the functions and properties of the active material and the support that their value in an electrode depends as much on how they are disposed with regard to each other, the electrolyte and the electrodes of opposite polarity, as it does on their relative proportions.

As large a surface as possible of the active material and as small a surface of the support should be in contact with the free electrolyte; preferably the entire support should be covered with active material, and the distance between it and the free electrolyte be the same at all parts.

The more nearly equal the distance of every portion of the active material from its support and the free electrolyte, the more uniform will be the distribution of the work; and those

which are furthest from the one should be nearest to the other, so as to average out the most favourable conditions.

It is also desirable that the distances between the surfaces of the active materials in opposing electrodes should be uniform, but this condition is not of nearly so much importance as the others and may well be sacrificed in their favour, for the resistance of the layers of free electrolyte plays an almost negligible part in determining the cell's behaviour.

Through-grid electrodes and electrodes with centrally-situated sheet conductors may be taken as representative of the two practical methods of arranging the active material and the support, and all the endless variety of designs that have been proposed may be considered as a modification of one or both of them. In the former the support is placed at the sides of the active material; in the latter at the back of it—considered in relation to the free electrolyte. The only other alternative is to put the conductor in front of the active material—that is, between it and the opposing electrode. Although its uselessness should be apparent, it has often been attempted with metallic case electrodes, but not liking to proceed to a logical extreme and entirely close in the active material, the case has generally been perforated.

Ribbed and grooved and also the strip supports belong to one or the other of the two classes, or combine something of each, according to their design and the method of their manufacture. When formed with a free acid space between their layers of active material they may be regarded as sheet electrodes with their support surfaces turned edgeways. When pasted they become grids with very elongated cells, but if there is a central core-plate they also conform slightly to the other type. In a shallow grid with a central core the idea of a conducting backing predominates, especially if the support is sunk well below the surface of the active material. In this way every make might be classified.

There can be little doubt that with regard to the conditions just laid down as most favourable for the electro-chemical requirements of electrodes, the central support is decidedly superior to the grid type. So far as the discharge reactions are not equally distributed throughout the electrode they will go on most vigorously at those parts most distant from the

support, and gradually extend inwards, thus not only avoiding the interposition of a layer of fully sulphated material of high resistance between the support and other portions not yet discharged, but, in the case of positive supports, their protective film of dense peroxide can only be attacked if the plate is quite exhausted. With grid supports the active material centrally situated within the pellets is at a great disadvantage compared with that at the sides, just in proportion to the size of the apertures, the thickness of the electrodes and the rapidity of the discharge rate; and it very readily becomes over-sulphated and ceases to take its share in the work of the cell. This is why, if the usage is severe, grid electrodes can seldom be kept up to their initial output unless they receive an amount of re-charging which very much reduces their efficiency.

The obvious advantage of grids is that they provide such a natural and easy method of maintaining the active material in its place. Here, as is so often the case in cell design and construction, the electrical and mechanical needs of the electrodes do not coincide, but it cannot be too strongly insisted that the more thoroughly the former can be satisfied the less will the latter require to be provided for. Under the best conditions formed active material holds together and in contact with the support by cohesion merely, because permanent external growth—the real disruptive agent—has been eliminated, or if it still occurs can do so without causing stress or strain; and this is the ideal that should always be kept in view. If the opposite course is adopted, of giving strength the first place at the expense of other considerations, not only will a poor electrode result, but its disintegration will most likely be actually hastened. An extreme example is furnished by the metallic case or envelope electrodes just now referred to. Their special purpose is to hold the active material so that it cannot possibly shift its position and escape from the electrode. To do this the support is deliberately placed where it can cut off from the active material as much as possible of the electrolyte, which is vital to its work; and half the surface, which might be most usefully employed if in contact with the active material, is left exposed to the free electrolyte—the most favourable position for its rapid peroxidation and for

dissipating the charging current in useless gassing. If the support is thin, it is soon eaten through; if thick, it is broken up from within by the active material, which cannot but become heavily sulphated and expand.

With most of the present used processes of preparing active material its cohesion is not generally such that it can dispense with a support so disposed as to relieve it from all shocks and jars and the strain of its own weight; and the grid electrodes still continue, therefore, to have the preference over those with only a central core. On the whole, the modern tendency is to discard or ignore all the elaborate and complicated designs for which such wonderful virtues have been claimed in the past, and to revert to the simplest and most fundamental types. The one new departure of recent years is the cast networks rather than grids now so largely employed as supports for pasted negatives. These allow the whole of the spongy lead to form one continuous mass throughout the support, and it cannot, therefore, so easily lose contact by shrinkage as in the grids with separate pellets; and this seems to be a decided improvement.

Electrolyte.

The strength of electrolyte that can be practically employed in lead cells ranges between solutions containing 15 to 40 per cent. by weight of pure sulphuric acid—that is, of specific gravities 1.100 to 1.300. If stronger, the sulphation and discharge of the spongy lead by local action becomes much too rapid; if weaker, the normal reactions between the active materials and the electrolyte may be modified in such a manner as to bring about abnormal sulphation, or the formation of “lead trees” and growths from plate to plate, due to small quantities of lead being dissolved and re-deposited. It will also be seen by reference to the curve of specific resistance of sulphuric acid solutions given on page 160, that their conductivity is at its best between the above mentioned limits, but falls off rapidly on either side of the loop of the curve in which they are included.

The volume of a mixture of sulphuric acid and water is less than that of its two components separately, and as the amount of shrinkage varies with the proportions of the

mixtures, it is not possible to merely calculate a table of their specific gravities. Several tables, differing slightly amongst themselves, have, however, been experimentally computed, and Otto's and Kolb's, given below, are the ones most generally relied on. Although the two tables cover the same ground they should both prove useful, because they are complementary to each other; the one being expressed in terms of the percentages

*Otto's Table of the Specific Gravities of Sulphuric Acid
Solutions at 15°C.*

Per cent. of H_2SO_4 .	Specific Gravity.	Per cent. of SO_3 .	Per cent. of H_2SO_4 .	Specific Gravity.	Per cent. of SO_3 .	Per cent. of H_2SO_4 .	Specific Gravity.	Per cent. of SO_3 .
1	1.0064	0.81	34	1.2560	27.75	67	1.5800	54.69
2	1.0130	1.63	35	1.2640	28.57	68	1.5920	55.59
3	1.0190	2.44	36	1.2720	29.38	69	1.6040	56.32
4	1.0256	3.26	37	1.2810	30.20	70	1.6150	57.14
5	1.0320	4.08	38	1.2890	31.02	71	1.6370	57.95
6	1.0390	4.89	39	1.2976	31.83	72	1.6390	58.77
7	1.0464	5.71	40	1.3060	32.65	73	1.6510	59.59
8	1.0536	6.53	41	1.3150	33.47	74	1.6630	60.40
9	1.0610	7.34	42	1.3240	34.28	75	1.6750	61.22
10	1.0680	8.16	43	1.3330	35.10	76	1.6860	62.04
11	1.0756	8.98	44	1.3420	35.82	77	1.6980	62.85
12	1.0830	9.79	45	1.3510	36.73	78	1.7100	63.67
13	1.0910	10.61	46	1.3610	37.55	79	1.7220	64.48
14	1.0980	11.42	47	1.3700	38.36	80	1.7340	65.30
15	1.1060	12.24	48	1.3790	39.18	81	1.7450	66.12
16	1.1136	13.06	49	1.3866	40.00	82	1.7560	66.94
17	1.1210	13.87	50	1.3980	40.81	83	1.7670	67.75
18	1.1290	14.69	51	1.4080	41.63	84	1.7770	68.57
19	1.1360	15.51	52	1.4180	42.45	85	1.7860	69.38
20	1.1440	16.32	53	1.4280	43.26	86	1.7940	70.10
21	1.1516	17.14	54	1.4380	44.07	87	1.8020	71.02
22	1.1590	17.95	55	1.4480	44.89	88	1.8090	71.83
23	1.1670	18.77	56	1.4586	45.71	89	1.8160	72.65
24	1.1740	19.58	57	1.4690	46.53	90	1.8220	73.47
25	1.1820	20.40	58	1.4800	47.34	91	1.8270	74.28
26	1.1900	21.22	59	1.4900	48.16	92	1.8310	75.10
27	1.1980	22.03	60	1.5010	48.98	93	1.8340	75.91
28	1.2066	22.85	61	1.5120	49.79	94	1.8356	76.73
29	1.2150	23.67	62	1.5230	50.61	95	1.8376	77.55
30	1.2230	24.49	63	1.5340	51.42	96	1.8384	78.36
31	1.2310	25.30	64	1.5450	52.24	97	1.8400	79.18
32	1.2390	26.12	65	1.5570	53.05	98	1.8406	80.00
33	1.2476	26.94	66	1.5780	53.87	99	1.8420	80.81
						100	1.8426	81.63

of pure acid present and the other in degrees Beaumé. Here, as is always the case with ordinary data regarding sulphuric acid solutions, the figures refer to weight, not volume of acid, but a curve based on Otto's table and showing the relationship between volume of acid and specific gravity will be found in Chapter IX.

Kolb's Table of the Specific Gravities of Sulphuric Acid Solutions at 15°C.

Degrees Baumé.	Specific Gravity.	Per cent. of H_2SO_4 .	Per cent. of SO_3 .	Degrees Baumé.	Specific Gravity.	Per cent. of H_2SO_4 .	Per cent. of SO_3 .
1	1.007	1.9	1.5	34	1.308	40.2	32.8
2	1.014	2.8	2.3	35	1.320	41.6	33.9
3	1.022	3.8	3.1	36	1.332	43.0	35.1
4	1.029	4.8	3.9	37	1.345	44.4	36.2
5	1.037	5.8	4.7	38	1.357	45.5	37.2
6	1.045	6.8	5.6	39	1.370	46.9	38.3
7	1.052	7.8	6.4	40	1.383	48.3	39.5
8	1.060	8.8	7.2	41	1.397	49.8	40.7
9	1.067	9.8	8.0	42	1.410	51.2	41.8
10	1.075	10.8	8.8	43	1.424	52.8	42.9
11	1.083	11.9	9.7	44	1.438	54.0	44.1
12	1.091	13.0	10.6	45	1.453	55.4	45.2
13	1.100	14.1	11.5	46	1.468	56.9	46.4
14	1.108	15.2	12.4	47	1.483	58.3	47.6
15	1.116	16.2	13.2	48	1.498	59.6	48.7
16	1.125	17.3	14.1	49	1.514	61.0	49.8
17	1.134	18.5	15.1	50	1.530	62.5	51.0
18	1.142	19.6	16.0	51	1.540	64.0	52.2
19	1.152	20.8	17.0	52	1.563	65.5	53.5
20	1.162	22.2	18.0	53	1.580	67.0	54.9
21	1.171	23.3	19.0	54	1.597	68.6	56.0
22	1.180	24.5	20.0	55	1.615	70.0	57.1
23	1.190	25.8	21.1	56	1.634	71.6	58.4
24	1.200	27.1	22.1	57	1.652	73.2	59.7
25	1.210	28.4	23.2	58	1.672	74.7	61.0
26	1.220	29.6	24.2	59	1.691	76.4	62.4
27	1.231	31.0	25.3	60	1.711	78.1	63.8
28	1.241	32.2	26.3	61	1.732	79.9	65.2
29	1.252	33.4	27.3	62	1.753	81.7	66.7
30	1.263	34.7	28.3	63	1.774	84.1	68.7
31	1.274	36.0	29.4	64	1.796	86.5	70.6
32	1.285	37.4	30.5	65	1.819	89.7	73.2
33	1.297	38.8	31.7	66	1.842	100.0	81.6

Every ampere-hour generated by a lead/lead peroxide cell involves the breaking up of 3.66 grammes or 0.129oz. or

0.008lb. of H_2SO_4 in the electrolyte; but a molecule of water is formed in the place of every molecule of acid destroyed, so the net result is simply an abstraction of sulphur trioxide, SO_3 , in the proportion of 2.98 grammes or 0.105oz. or 0.0066lb. per ampere-hour. As the electrolyte must still contain sufficient acid at the end of the discharge to keep the final specific gravity above 1.100 at least, it is evident that a much larger quantity has to be provided than corresponds to these ampere-hour equivalents. The writer has found the following formulæ very useful for calculating the necessary weight of dilute acid of any given initial strength, and which shall discharge down to any other given final strength.

P is the percentage weight of SO_3 initially present, and p the percentage weight finally remaining in the electrolyte. These data for any given specific gravity can be obtained from the tables.

s is the ampere-hour equivalent of SO_3 as given above.

O is the output in ampere-hours.

$$\text{Weight of dilute acid per ampere-hour} = s \left(\frac{100 - p}{P - p} \right),$$

$$= 0.0066\text{lb.} \times \left(\frac{100 - p}{P - p} \right).$$

$$\text{Total weight of dilute acid} = Os \left(\frac{100 - p}{P - p} \right),$$

$$= 0.0066\text{lb.} \times O \left(\frac{100 - p}{P - p} \right).$$

If the percentage weights and ampere-hour equivalents of H_2SO_4 are substituted for those of SO_3 in the above equations, an error is introduced through thus ignoring the water set free during the discharge, but they are absolutely correct in the form given.

Having determined the weight of acid in pounds, its volume in gallons can be ascertained by dividing by ten times the initial specific gravity, or its weight in kilos can be converted into volume in litres by dividing by the initial specific gravity merely.

The electrolyte in the pores of the active materials will always be weaker on discharge and stronger on recharge than

that in the body of the cell where the hydrometer readings are taken; and the denser or thicker the layers of active material or the higher the current rate the more pronounced must these differences be. For this reason it is not advisable that the strength of acid should approach too close to either of the limiting densities at any stage of working, and it would seem preferable for the variations of specific gravity to take place round the median figure. There is, however, little doubt that the tendency to abnormal sulphation does show a marked increase with strengths of acid much above 1.200, and the usual practice is to make that the maximum density.

The question of quantity of electrolyte does not need much consideration in stationary cells. The electrodes having been mounted in a box of suitable size to allow a proper distance between them and a sufficient depth for the accumulation of loose material below their bottom edges, a space remains to be filled with liquid, and its dimensions determine the amount of acid and the fall of specific gravity during discharge. As a rule, the former works out at about 5 to 10 ampere-hours per pound of 1.200 acid, the latter at 0.030, giving a final strength of about 1.170, but if the room has been cut fine the drop may be as much as 0.050. In no case should the density be less than 1.150 at the end of a complete normal discharge, or otherwise the electrolyte may be too much weakened—possibly even to the extent of having the whole of its acid abstracted—if by any chance the discharge is abnormally prolonged and the cells run dead out.

As the strength of acid employed in a cell is raised from 1.200 to 1.300 density, the initial and average P.D.s of discharge are distinctly augmented. More than one investigation, however, which has been made into the effects of variations of acid strength upon output goes to show that the ampere-hours reach a maximum at some specific gravity between 1.150 and 1.200, and rapidly decline above the latter figure. Even after the increased viscosity and electrical resistance of the stronger acids is taken into account, the result is not altogether what might have been expected, but at any rate it confirms the desirability of keeping down the strength of the electrolyte.

Position of Electrodes.

It is always customary to arrange the electrodes in a cell with a negative at either end. If there were an equal number of plates of each kind, so that one end finished with a positive, this would very soon buckle badly owing to unequal expansion caused by its doing work at one face only. Even as it is the end positives often give more trouble than the rest under bad treatment, because they have the whole of the outside negative to discharge against at the one side, while on the other they have to share the negative with the next positive. To overcome this trouble makers frequently employ end negatives half the thickness and output of the others, and this is certainly the correct practice, especially if the plates are of a type not having a central metallic core, which separates the active material and electrolyte on either side.

Separating.

At one time positives and negatives used not to be kept more than 0.25in. apart, with the idea of reducing the intervening layers of electrolyte, and, therefore, the internal resistance of the cell, as much as possible. It was, however, found that the output could actually be increased by putting the plates at a greater distance, the fact being that the larger bulk of solution thus brought into close proximity to the active material was better able to maintain the strength of acid within its pores; and the higher P.D. consequent upon the diminution of polarisation more than compensated for a slight loss in other directions. Nowadays, about 0.5in. is the most usual spacing, and even that may with advantage be somewhat increased when very rapid discharge rates have to be dealt with. Incidentally, a wide spacing also lessens the liability for loose scale or detached pieces of active material to lodge between the plates and short-circuit them.

Stout glass tubes make the best distance pieces. They should be long enough to reach right down to and stand upon the floor of the cell rather than hanging from the upper edges of the plates by lips, for if one drops through it is troublesome to recover, and may very easily fracture a glass box should it strike the bottom sharply.

If it is bad not to have a wide enough acid space between the electrodes, it must be worse deliberately to fill up with obstructions what space there is or to keep the electrolyte from contact with the active materials. This, however, is what the "protected" electrodes, which had such a vogue a few years back, amounted to. The poor positives, which most need a free supply of acid, were plastered up with sheets of asbestos held in position by grids of ebonite or earthenware, or perforated cases of celluloid or ebonite were employed either with or without such layers of porous fabric.

One firm having started the fashion, others followed suit, and it took some time before they realised that this was only another variant on the old fallacy of trying to forcibly control the active material by limiting the conditions vital to its usefulness. Actually, protection aggravates the very troubles it is intended to overcome and is quite unsuited to stationary cells, where durability is essential and weight not of first importance, for under these circumstances any active material that cannot retain its place on the support without such assistance had much better be peacefully reposing at the bottom of the box. In light-weight cells protection may be tolerated or even be indispensable, but then only as a necessary evil.

Supporting.

Both sets of electrodes cannot be stood directly upon the bottom of their cell box, because the first film of detached material that collected there would set up leakage between them, which would soon develop into a more or less thorough short circuit. In some cases one set—generally the negatives—is supported from the bottom by means of prolongations or lugs, which are burned into flat connecting bars, and the positives are hung from the sides or top of the negatives, some arrangement of insulating material, such as saddle-pieces, being used to prevent them from coming into metallic contact. Another plan is to raise up both the negatives and positives and to let them rest upon wedge-shaped strips of paraffined wood placed on the floor of the cell. The sides of the strips must slope away pretty steeply from the edge which supports the plates, otherwise the falling material will

be very liable to lodge there, and, in any case, this danger cannot be altogether obviated.

It is now becoming more usual to support the electrodes from lugs high up on their sides upon two stout glass slabs set vertically in the cell upon rubber shoes, which form a flexible bed between themselves and the bottom of the box. By this means an absolutely clear space of any desired depth for the accumulation of the deposit is easily secured below the plates, while the surfaces of the supporting pieces are so disposed that it is practically impossible for any considerable leakage to take place across them. It is probable, however, that some loss must occur over any horizontal surface beneath the liquid and in contact with both sets of electrodes owing to the slight coating of metallic particles that is sure to be deposited upon it, so the supporting lugs are sometimes brought well up above the top edge of the plates, and rest upon slabs high enough to project beyond the level of the electrolyte. From this it is a short step to hanging them on the edges of the containing box itself, or, in the case of lead-lined wood boxes, upon glass rods placed upon its edges, provided the boxes, when of glass, are strong enough to take the strain. This method seems to be the acme of simplicity, efficiency and cheapness, and is now very largely adopted.

Automobile Cells.

Cells intended for use in electric automobiles—which appears to be the only direction where an opening is left for their extensive application to traction purposes when carried on the moving body—have to be designed and estimated in accordance with quite a different standard of requirements to what holds good for stationary batteries. They may be roughly divided into two classes: Those having an output of 3 to 5 ampere-hours per pound of complete cell and a moderate durability—little less, if used under similar conditions, than that of lighting cells; and those whose life takes quite a secondary place as compared with their output for weight, which may be anything up to about 12 ampere-hours per pound at slow discharge rates.

The weight of a cell is cut down to a minimum by a combination of three methods. First, by securing the highest

possible specific output from the active material ; second, by employing an electrolyte as strong as one dare, and working through a very wide range of specific gravity, that is to say, eliminating the bulk of the water and surplus acid ; third, by reducing the support, which contributes nothing to the output, to the smallest proportions. Besides this, the connecting lugs, containing box, and any parts used in mounting and separating the electrodes, must of course be no heavier than is absolutely necessary.

On referring to the table given on page 271, it will be seen that the gain of output by further diminishing the weight of the support to less than one-third that of the total weight of electrode is not great, even on the assumption that the specific output of the active materials remains the same under these circumstances ; and, as this involves serious constructional difficulties in also maintaining the coefficient of support surface, it is hardly worth striving after. The weight ratio of active material to support in the lightest electrodes ranges from 1 : 1 to 2 : 1. If the plates do not much exceed $\frac{1}{8}$ in. in thickness they should when new yield a specific output of about 30 ampere-hours per pound of active material at moderate rates, and with the larger proportion of support this might possibly be increased towards the maximum of 45 to 50 ampere-hours per pound. How long these results will last, and how fast and far they will deteriorate, chiefly depends on the quality of the active material, on the extent to which the subdivision and distribution of the support throughout its active material has been provided for in the design, on the treatment, and on the strength of the electrolyte. This latter, as was said earlier in this chapter, cannot safely be allowed to exceed 1.300 or to fall below 1.100.

On the basis of these figures the possible outputs for weight of a cell can readily be approximately computed. If the specific output of the active material is taken as 30 ampere-hours per pound, and its ratio to the support as 1 : 1, then 2lb. of positive electrode, 2lb. of negative electrode and 1lb. of 1.300 acid, discharging down to 1.180, will yield 30 ampere-hours, or 6 ampere-hours per pound. If the ratio of active material to support is as 2 : 1, only $1\frac{1}{2}$ lb. each of positive and negative electrodes will be required for the same output,

making 4lb. with acid, or 7.5 ampere-hours per pound total. Finally, if the previous ratio is readopted, but the specific output of the active material now assumed to be up to its maximum value, or 50 per cent. higher than before, only 2.66lb. of electrodes are necessary, and the output is slightly over 8 ampere-hours per pound.

It is not essential that the positives and negatives should be exactly alike in design and proportion. The latter are often slighter and thinner, but in each case it may still be presumed that the relation between their united weights and the output will not be much affected.

The amount of dilute acid is calculated by the formula given on page 280, as follows:—

$$\text{Weight of acid} = 0.0066\text{lb.} \times 30 \times \frac{100 - 15}{82 - 15} = 1.0\text{lb.}$$

It will occupy about 20 cubic in., a space not much greater than what is required by the electrodes themselves, so that, after the necessary clearance has been allowed for at the bottom of the box, the distance between the plates must not exceed their own thickness, or even less should there be any amount of free acid beyond their side and top edges. In practice $\frac{1}{8}$ in. to $\frac{1}{4}$ in. is about the usual spacing for the lightest and most compact cells, and under these conditions their bulk will not be more than about 1 cubic in. per ampere-hour, exclusive of what room may be considered necessary above the top of the electrodes for spare electrolyte, connecting bars, lugs, &c., and to avoid loss by splashing.

No account has been taken in the above figures of the weight of the containing box and separators. For cells of over 100 ampere-hours output this should not be more than 5 to 10 per cent. of the total, and if things are being cut very fine it can be offset against a further saving in the weight of the electrolyte. There seems little doubt that in cells containing small quantities of very strong acid, the consumption on discharge is less than is required by the usual theory, owing to the hydrated peroxide entering into combination with a considerable percentage of H_2SO_4 . The Author came to this conclusion some years ago, although he has never had an opportunity of properly investigating it,

but he has since found that it is confirmed by the experience of others besides himself.

The proportions assumed to exist between the weights of the active materials, supports and the electrolyte can also be slightly varied in other ways, but a further saving in any one of them generally means an increase of weight elsewhere. Only by a combination of the highest specific output of active material with a minimum of support—a most difficult problem—is it possible to much exceed an output of about 8 ampere-hours per pound of cell, and when it is claimed that the higher limit of 12 ampere-hours has been approached, it would be interesting to know how long and under what circumstances it can be retained.

It is often stated that the large outputs for weight now furnished by autocar cells would have been quite impossible a few years ago, and the improvement is generally ascribed to new methods of construction. There seems to be but little justification for these assertions. In this connection, it is extremely interesting to recall some figures published in 1888, by Emile Reynier, concerning the capabilities of the Faure-Sellon-Volckmar accumulators. He described three types of cell: one of considerable weight, for stationary use; another, having an output of 4.2 ampere-hours per pound at a six-hour rate, much like the heavier of the modern traction cells; and a third, with which we are here chiefly concerned, whose output was as high as 7.5 ampere-hours per pound at an eight-hour rate. The electrodes were of the grid type, 2mm., or about $\frac{1}{12}$ in. thick, and consisted of equal weights of support and active material, and the specific output of the latter was 45 ampere-hours per pound. The strength of the electrolyte is not mentioned, but it is evident from the small quantity employed, that it must have been worked through a wide range of specific gravity. The cell had an output of 155 ampere-hours and weighed 9.7 kilos, or 21.4lb. total, so it was in this respect fully the equal of nearly all the light-weight cells of the present day, and, with the exception, perhaps, of the method of separating the electrodes, embodied every essential feature of their construction. Certainly nothing is said as to its life, but it could not well have been less than many of those since claimed to be going to revolutionise the industry.

As a matter of fact, the attainment of big outputs for weight is in no wise associated with any particular mode of construction. It may be arrived at by suitably modifying the proportions of parts in the most ordinary types, and of the various makes the best will not necessarily be that which gives slightly more ampere hours per pound than the others. Their relative merits cannot be determined without taking life and depreciation into account, and this depends on a correct application of the fundamental principles of design, and then on the method of manufacture, or, in other words, the quality of the active material. It is in the latter respect that many types, nominally much alike, really differ, and in this direction that any considerable further improvements must be looked for.

There can be no disputing that, as a general principle, the rate of depreciation of a cell increases with its output for weight, but what is the exact relation between them or what the life of the extremely light cells sometimes used in automobiles it is very difficult to say, either *a priori* or as a result of experience, the matter being so complicated by varying conditions of treatment. Apparently, in the lightest cells an average life of six months, with a very liberal allowance for loss of out-put during that period, seems to be the accepted standard for positives rather than the three to five years required if in stationary cells; and the durability of the negatives is also reduced in the same proportion. Accompanying and, indeed, almost essential to this change of view and of working conditions, maintenance is carried out on a different system, and methods of manufacture are revised so as to secure a fuller utilisation of old material. The idea is to work the cheapest and lightest possible battery for a short time only. Then, as soon as it begins to give trouble or seriously diminish in output, without spending time in patching it up, to scrap the electrodes and put in entirely new sections, not even attempting to work the old negatives with fresh positives. This plan has before now been considered in connection with both electric trams and launches, but circumstances have not hitherto enabled it to receive a fair trial in practice. Pending a satisfactory demonstration of what can be accomplished on such lines men think that in

the long run better results are to be obtained from the use of a heavier make of traction cell, but of longer life, rather than from those in which weight is reduced regardless of all other considerations.

The design of cells of this type is in nearly every respect a compromise between the stationary and the lightest traction cells. The weight of the supports equals or exceeds that of the active material; indeed, Planté-type positives may even be used if they are heavily formed or the support is very thoroughly subdivided. The electrodes are not of such extreme thinness, and the electrolyte though limited is not cut down to the utmost. The output of the cells generally works out at 3 to 5 ampere-hours per pound complete, and about 2 cubic in. per ampere-hour.

Owing to the very narrow spacing between the plates of automobile cells, both of the light and heavy kinds, it is generally necessary to employ some form of protective separation which will prevent their being short circuited by detached active material, and perhaps help to support the electrodes themselves. Porous or perforated sheets and casings of asbestos, cellulose, wood, earthenware, ebonite, celluloid and other substances have been tried, either alone or in combination with many kinds of separating devices, but thin sheets of perforated ebonite, either corrugated or placed flat against the positive with thin spacing ribs on the other side, have proved most satisfactory. In America grooved wood diaphragms have been combined with the latter with good results. The one thing to be avoided is celluloid. It has been extensively used on account of the advantages it offers in many ways, and every one in turn has thought he has discovered the one brand which will resist the action of the electrolyte, but in the end it has always had to be given up.

CHAPTER VII.

THE MANUFACTURE OF LEAD CELLS.

Supports are always constructed either of pure soft lead or of hard lead; that is, lead alloyed with a small quantity of antimony. Even a fraction of 1 per cent. of antimony will impart a considerable hardness, which increases with the amount added; but not more than from 2 to 5 per cent. is generally used, else the electrodes become too brittle. Although enhanced rigidity is the chief reason for employing antimonial lead, supports made of the alloy are also claimed to be less rapidly oxidised by local action than when composed of the pure metal. Certainly they cannot be successfully peroxidised to any depth by an ordinary formation process, but in use they sometimes appear to undergo a deterioration of strength which is equally fatal to their durability. There is also some doubt as to whether antimony cannot be dissolved out of positive supports by the electrolyte, and set up local action at the negative by re-deposition in the porous lead. L. Jumau has made experiments and maintains that such is the case.* Any antimonious oxide, Sb_2O_3 , formed at the positives would no doubt behave in this way, because its sulphate is slightly soluble in dilute sulphuric acid, but if, as is more probable, the metal passes to the higher stage of oxidation, Sb_2O_5 , (antimonic acid), it does not seem so likely that it would undergo any further alteration.

A further question that needs consideration is how far antimony affects the electrical resistance of the supports. Pure lead is none too good a conductor; antimony is a very

* *L'Eclairage Electrique*, Vol. XVI., p. 133, July 23, 1893.

poor one, and its presence must impart a high specific resistance to the alloy. But on this point no definite information is to be had, nor on another of even more importance—namely, the conductivity at the surfaces of contact between the support and the active material. In the case of pure lead the two blend and hold together to the degree which indicates that the intimacy of contact must be very great. In the case of hard lead, not only is the cohesion less, but it seems very probable that the oxide of antimony may add to the resistance of the lead peroxide.

Apart from all these possible objections, it has already been pointed out that too much strength and rigidity are frequently the reverse of desirable qualities in a positive support, and in such event the addition of antimony to the lead may be worse than useless. For instance, grids of alloy are often broken up and destroyed by the expansion of the active material, when, had they been of soft lead, they would have stretched a little without suffering any damage. Antimonious lead has, however, been successfully employed in some well-known types of positives which are of rather exceptional design. It is more often introduced into negative electrodes, for some of the objections just enumerated do not then arise and its merits are more apparent.

Commercial lead is one of the purest of metals. The processes for its desilverisation have been brought to such a pitch of perfection that practically the whole of the silver is removed; and most of the other impurities, such as sulphur, arsenic, zinc, iron, copper and antimony are oxidised out by prolonged and careful roasting. From the battery maker's point of view, the importance of the lead used for the supports being of the utmost degree of purity cannot be too strongly insisted upon, and ordinary soft lead, pure as it is, frequently fails to come up to the standard of his requirements. The primary and most serious result of the presence of impurities in quantities so small that they would usually be considered quite negligible, is to reduce the durability and shorten the life of the positive supports by rendering them liable to be rapidly corroded and oxidised by local action; while the impurities soon pass into solution and, according to their nature, may or may not give rise to secondary effects. That these

things should happen if the traces of foreign materials were in true combination or alloy with the lead, and uniformly distributed throughout its substance, is hardly conceivable; and the explanation must be sought on other than purely chemical lines.

It is well known that the addition of a very minute percentage of many metals has a most marked effect upon the structure of pure solid lead, as is shown by the alteration in its hardness, tenacity, colour, fracture and the texture of its surface; and that its tendency to crystallise on cooling becomes much more pronounced. These facts, considered in conjunction with the principles upon which the desilverisation of lead by Pattison's and by Parkes' processes is based, and the differences exhibited by the pure or impure molten metal in its behaviour as regards atmospheric oxidisation, all suggest that castings of the latter may not possess a homogeneous structure and composition, but consist, in reality, of a mass of crystals of pure lead embedded in a matrix of some alloy which contains the bulk, if not the whole of the impurities. In short, the metal may undergo a sort of liquation in the act of solidifying, and the pure lead settle out, first, from an alloy of slightly lower melting point; and although this alloy may be quite insignificant in amount—the merest film between the crystals—it will ramify through every part of the casting. It is easy to see that supports of this nature would be readily attacked and penetrated wherever the alloy was to be found, and on this view of the matter both their disintegration and the rapid solution of the impurities may be accounted for. It would also follow that comparatively impure lead might give excellent results if cast under conditions which did not allow of its crystallisation or liquation, and this is quite in accordance with the erratic way in which troubles apparently due to impurities often crop up without the quality of the metal having undergone any alteration; the real cause being some slight and unnoticed change in the details connected with the preparation of the support.

Manufacturers differ somewhat in their ideas as to the maximum percentage of impurity which is permissible in the lead they employ, and this, no doubt, is partly justified by the varying nature of the type and design of the electrodes they

construct; but, as a rule, it is wisest to avoid all risks, and not to sacrifice purity for the sake of saving a few shillings per ton. The metal cannot, of course, be obtained absolutely pure, but it need not be far off, and lead which yields well over 99·9 per cent. *by actual assay*, is generally procurable in large quantities at reasonable prices; while the amount of any single impurity present is less than 0·001 per cent. Copper is a most frequent contamination, and is generally credited with being the one most dangerous to the life of the electrodes, even if it does not exceed 0·01 per cent.; and if the physical explanation just suggested is allowed, it may well be that lead crystallises more readily from an alloy with copper than with some of the other metals. The injurious effects of copper are not confined to the positive electrodes, for having once passed into solution it is quickly re-deposited on the negative active material, and there sets up a continuous local action which prevents the cell from retaining its charge on open circuit and leads to abnormal sulphation and permanent loss of capacity. In these respects also, copper seems to be pre-eminent over most other of the usual impurities.

Lead often contains small quantities of antimony, owing to its having been imperfectly softened or refined; and in this connection it is advisable to bear in mind that because lead can form a homogeneous non-crystalline alloy with antimony in small or moderate proportions, it does not follow that it will do so with mere traces. Indeed, if one can judge from the effect of antimony, under such circumstances, upon the mechanical and visible properties of lead, its presence is more to be feared than that of copper. The question as to the solubility of antimony in the electrolyte has already been touched upon.

The chemical examination of samples of lead is not a case where rough and ready tests will suffice, for, considering the smallness of the impurity to be dealt with and the importance of accuracy in the results, it should only be entrusted to an analytical chemist of skill and experience. It is not usual, nor necessary, to attempt to determine the amounts of the traces of all the many substances into which the total impurity can generally be split up. Copper, iron and antimony are estimated; arsenic, tin, zinc, nickel, bismuth, silver, and so

forth, may be separated and their presence noted, or they may be ignored altogether; but if there is cause to suspect that any one of these substances exceeded 0·001 per cent. further enquiry would probably be necessary.

The art of casting lead supports of complicated design, and with the metal subdivided into extremely slight portions so as to afford a very large exposed surface, has, within the last few years, been brought to a pitch of perfection quite undreamed of in the early days of the industry; and in this respect the German manufacturers, headed by the old Tudor Company, have been especially to the front. The casting is always made in metal moulds or "chills." For the simple forms of grid first introduced a two-part mould, opening on hinges and having suitably arranged and exactly corresponding grooves cut on the adjacent surfaces, was all that was necessary; and moulds of this kind are still largely employed. To ensure the easy withdrawal of the casting from the mould the grooves in the latter are somewhat V-shape and have sloping walls which make the recesses in the support smaller at its centre than its surfaces; and this, in the case of pasted grid electrodes, has the additional advantage of keying in the pellets of active material, unless they split in the middle. If "through" plates are not required, but supports with a web of solid metal down the centre, as is usual with grooved electrodes, then the two faces of the mould are cut away except at their edges, or else spaced apart by a liner of the right thickness. If very fine and deep ribs have to be produced the moulds are built up of a number of small separate sections held in a frame, and their construction then becomes a costly and difficult matter.

It is not necessary to attempt to describe and discuss the variety of elaborate moulds or machines that may be used to cast grid supports, for in almost every case they are bound up with some special firm or system. Their purpose is always the accomplishment of one or both of the following objects:—Grids with undercut or inwardly tapering ribs, so as to give a firmer grip on the active material; and grids with double lattices and internal spaces, or with alternate lattices on either side, so as to obtain a continuous mass of active material, increase its weight relatively to that of the support,

and improve the subdivision of the one by the other. Some examples of such grids have already been illustrated in Figs. 20 to 25. The means generally adopted are to make the two halves of the mould interlocking—that is to say, with projections on the one fitting into recesses in the other—and to draw them apart diagonally instead of at right angles to the plane of the plate; but these principles are very variously worked out. In some cases the mould consists of more than two parts, in others core pieces are used, and so forth.

It is by no means easy to cast intricate and finely-ribbed supports so that the metal shall be perfectly sound and homogeneous at every part of them, and the difficulty rapidly increases with the size of the electrode. If the lead is not of the purest, success is almost impossible, for the metal tears on attempting to withdraw the casting from the mould; or, even if this does not happen, it will be found to be porous and brittle in places. The removal of the casting is generally aided by the use of some lubricant, such as finely-powdered mica, plumbago or French chalk lightly dusted into the mould before pouring in the metal. A certain amount of pressure, which may be regulated by the head of metal, will have to be put upon the lead to force it to the extremity of the smaller interstices, and both the melting-pot and the mould must be kept at a sufficiently high temperature to prevent it from solidifying prematurely. It is needless to say that every precaution must be taken to prevent scum or dross from entering the chill. For large and difficult plates, runners may have to be provided to admit the metal to the casting proper at more than one point, and the escape of air must be also allowed for.

Besides casting supports, there are many other methods of preparing them from rolled, drawn or “squirted” lead, in the shape of sheet, strip or wire. Such as may be of interest are described elsewhere under the names of those who practise, or have practised, them; but it is of interest to note here that all these forms of lead must be denser and more homogeneous, and therefore more durable, than the cast metal. The latter is certainly the first stage of rolled and drawn metal, but during those processes a true flow takes

place which seems to entirely obliterate its crystalline structure and blend it into a uniform substance. The very merits of the denser metal are indeed the reason why its use is often avoided if it is going to be electro-chemically formed, as it offers much greater resistance to oxidation to any depth than cast lead, and this is significant testimony.

When the mechanical construction of the supports, cast or otherwise, is completed, they are generally ready to be formed or to receive the raw active material, but occasionally they undergo a preliminary treatment to thoroughly cleanse their surfaces and ensure a perfect and uniform contact between every part of the support and the active material. It may consist of a purely mechanical operation, such as scratch-brushing or the action of a sandblast; or, when grease is likely to be present, as is often the case with drawn or rolled metal, of a pickling in caustic alkali solution; or of a surface peroxidisation of negative supports, before pasting, by charging as positives in dilute sulphuric acid for a short time.

Active Material.

All the processes for preparing active material may be placed in one or other of the three following classes:—

Metallic lead—generally the support itself—is oxidised and electrolytically converted into lead peroxide, either in dilute sulphuric acid or in a special solution.

Solutions of soluble salts of lead are electrolysed, or else lead compounds—such as the sulphate, carbonate or chloride—are reduced direct from the solid state in some special solution in which they are sparingly soluble. In either case the porous metal is almost invariably obtained in too loose a condition to be available as active material until it has been subjected to a special treatment to compress and cause it to adhere to the support. Spongy lead prepared from cast lead chloride does not, however, require such consolidating if a little zinc chloride has been admixed with the raw material to promote a crystalline structure.

Lead oxides are applied—usually in the form of a paste—to the supports, and electrolytically oxidised or reduced in the ordinary sulphuric acid. It is the exception for a special electrolyte to be employed.

Only positive active material can be directly produced by the first of the above methods, but it may then be converted into negative material by reversal. The second method yields negative active material directly (lead peroxide can be deposited direct from certain solutions, but satisfactory active material has never yet been obtained in that way) or positive material by reversal; but, by the third method, either positive or negative material may be directly prepared. The first method is the oldest, being the one by whose means Planté obtained the earliest reversible lead cells, and he it was who introduced the term "formation" to describe it, and also wrote of this type of electrodes as "formed" plates. In return, all formed electrodes are commonly called "Planté type" or "Planté formed"; but where his original process of formation in dilute sulphuric acid only is referred to here it will be spoken of as a true Planté formation. The use of the word "formation" has now been extended to all electrolytic processes connected with the production of active material, whether of the formed, pasted or other type.

Nowadays the preparation of active material from lead oxides appears to be such an obvious, quick and simple process that it may seem strange why Planté did not make use of it many years prior to Faure's discovery.* But, apart from the fact that until the arrival of the dynamo, and so long as galvanic cells were the only prime source of electricity in any considerable quantity, there was little point or purpose in searching for means of commercial storage, the method is not really at all obvious. Considering the state of knowledge at the time, the deposition of spongy lead from a solution of some soluble salt would suggest itself as the most likely alternative method of formation, and that Planté tried. Faure himself does not appear to have got much beyond this stage when he applied for his first and most important patent in 1881, for he speaks quite indifferently of using "oxides or other salts of lead"; selects as his typical raw active

* It has, indeed, been stated by some French writers that Planté had practised this method, and abandoned it because he could not maintain the active material in contact with the support; but Planté himself does not appear to have mentioned it in any of his publications.

material a mixture of lead sulphate and pulverised coke stuck together with a solution of gelatine (sawdust might sometimes be added); and only contemplates peroxidising his active material after it has first been reduced to spongy metal. In fact, all he seems to have had in his mind at that time were very crude processes of the second class; and the use of red lead is not specifically mentioned until his next patent was filed a few months later.

The rapid and perfect electrolytic reduction of litharge and red lead in an electrolyte in which they are practically insoluble, is not a result that might be anticipated from analogy with any other of the ordinary lead compounds, while their peroxidisation under similar conditions is still more anomalous; and it is for this reason that these methods of preparing active material are placed in a class by themselves. A third distinctive feature of the oxides in a state of powder is their power, when mixed with a solution of sulphuric acid, of presently setting to a continuous mass which retains its cohesive properties after it has been converted into metallic lead or lead peroxide; but this behaviour could also not have been produced from any *a priori* considerations. No doubt it partly accounts for their easy electrolytic decomposition; but, whether this is so or not, without it the pasted types of electrode could never have rivalled those whose active material was prepared from the support itself.

Planté Formation.

On passing a current between two clean plates of lead immersed in dilute sulphuric acid, the positive almost immediately gives off oxygen gas and becomes covered with a film of lead peroxide. If the electrolyte is quite pure and the surface of the metal free from oxide, the film is perfectly transparent and so thin that its brown colour is barely perceptible; and it is very important to note that, so long as the current is maintained, it shows no increase in thickness whatever. Directly the circuit is broken the peroxide is reduced by the lead underneath, both becoming sulphated, and this change is practically instantaneous, as may be seen by watching the rapid fading of the brown colour of the electrode. On again applying the current, the newly sulphated

metal is now peroxidised in addition to that originally attacked, so the film is a little thicker than before and exhibits a slightly darker colour; and by repeating this procedure a few times it attains to a fine orange brown, but still perfectly transparent, like a skin of varnish, through which every marking underneath can be clearly distinguished.

The local action on open circuit may be considered as a case of the ordinary discharge reactions taking place between two electrodes, one of which is the layer of peroxide and the other the lead support in contact therewith. It will be found that after each additional re-charge the colour of the peroxide changes more and more slowly. This does not of itself prove that the local action is diminishing, because as the layer of peroxide increases it could re-act with the same quantity of lead as at first without being nearly so heavily sulphated; but by measuring the output of the electrode it can easily be ascertained that its capacity soon becomes stationary unless the periods of rest are rapidly lengthened from minutes to hours, then to days, and ultimately even to weeks. A very natural explanation of this behaviour can be supplied. The peroxide cannot attack the metal without there is an electrolyte in contact with both of them. To begin with, the excessively thin film of gelatinous or colloidal and hydrated peroxide—for that, from its appearances, must be its condition—itself transmits the small amount of moisture required; but, as the layer thickens, less and less passes through, until the surface of the lead approximates to a state of dryness, and its oxidation can only proceed at a rate which is strictly limited by the rate of transfusion from outside.

To expedite the formation and compress the time required for its completion within anything like reasonable limits, it soon becomes necessary to open up the peroxide so that the acid can penetrate through it more easily, and this is done by fully discharging the electrodes after each recharge instead of leaving them on open circuit. Under this treatment the smooth transparent colloidal peroxide is gradually changed to an opaque and rough crystalline layer, and the formation proceeds much more rapidly for a time; but ultimately it slows up again until a stage is reached beyond which any

further increase of capacity becomes too long and expensive a matter to be commercially feasible. Great care has to be exercised in the earlier stages of the formation to prevent a more thorough opening up of the peroxide taking place than is desired, for it is extremely liable to peel away in flakes and leave the bare metal on which operations have to begin afresh.

Reversals of the positive electrodes during formation are in no way essential to Planté's process. He practised it, and with his type of cell and conditions of working it was the only convenient method; but on a large practical scale, even if both the positives and negatives are to be formed, it is more economical of time and current to form the whole of them as positives against dummy plates, and then finally reverse those intended for negatives; while, if only the positives require forming, reversals would be quite purposeless. Negative electrodes undergo no formation as negatives, and acquire no capacity beyond what may be due to the reduction of any oxide originally present on their surface. It would not be unreasonable to suppose that a further portion of the solid metal might be sulphated each time a negative was discharged, and then reduced to spongy lead on the following recharge, so that in this way a layer of active material would gradually be formed. Planté was, indeed, under the impression that something of this nature actually occurred, but it has proved not to be the case. Negatives whose active material is prepared from their own support are in all cases simply reversed positives, so they will not require to be considered separately.

Quick Formation Processes.

The object of all the various methods of formation that have been introduced since Planté's time is to do away with the long rests on open circuit or the frequent discharges. To accomplish this result it is necessary to postpone the production of the protective film of peroxide on the surface of the plate until an amount of lead sufficient to furnish the required capacity has been attacked. According to some methods the lead is first oxidised, either chemically or electrolytically, and then this oxidised compound is electrolytically peroxidised by an entirely separate treatment; more usually, the two actions proceed simultaneously as part of the same operation, but the

one always somewhat in advance of the other. The latter effect may, for instance, be obtained by forming the electrodes in dilute sulphuric acid to which a salt of some other acid, such as nitric or acetic acid, has been added. The passage of a current does not now immediately produce a film of peroxide on the positives as when sulphuric acid alone is used, but they are first rapidly coated with a layer of some opaque, white or gray-white lead compound, and then crystalline peroxide makes its appearance and steadily increases in quantity, for in this condition it has to acquire a considerable thickness before it seriously impedes the electrolytic attack on the underlying metal. It seems pretty certain that throughout the formation lead is never directly converted into peroxide, but first assumes a monoxidised stage for a short time. Some evidence of a thin layer of this intermediate compound can always be found adhering to the plate if the covering peroxide is removed, and often the white compound is present in sufficient quantity to show up without this being done. One of the first requirements of a successful formation is to so adjust the various conditions that the oxidising and peroxidising actions both proceed at about the same rate. If the oxidising power of the electrolyte is too strong, or the forming current too weak, large quantities of heavily sulphated material may be produced which cannot be properly peroxidised afterwards and converted into an efficient active material, while, at the same time, the electrodes will be deeply corroded to no purpose. If, on the other hand, the peroxidisation predominates, by reason of an excessive current rate or other causes, then the layer of oxidised material gradually diminishes, until finally the action gets back to the metal itself, a film of colloidal peroxide is formed just as in the Planté process, and the formation will be brought to a premature conclusion. It is in this way, indeed, that every formation must eventually be finished, otherwise it might continue after the electrodes had left the factory; but once they have been "sealed off," whether unintentionally or not, it is generally impossible to get a satisfactory quick formation to commence again. All the same, electrodes which have been imperfectly sealed off may easily retain enough foreign acids to bring about their speedy

destruction when put to work, and in practice this often occurs.

It is not at all clear why the alteration of electrolytic action which renders quick formation possible should be brought about by the presence of other acids in the sulphuric acid solution, or what are the special properties which enable them to modify it. No doubt the solubility of the compounds they can form with lead is an important factor; although lead should never appear in the solution during formation, otherwise it will be reduced to loose spongy metal at the negatives and may cause no end of trouble. The white material produced at the positives is apparently some hydrated basic salt, and the power of readily forming such compounds may in itself be one of the necessary requisites for a successful electrolyte. Sulphuric acid is rather exceptional in not easily entering into basic combinations with lead, and the insolubility of the lead sulphates is well known. A third property, which may also be very material, is that of freely passing between two or more degrees of oxidation. Nitric and chloric acids, for instance, can both be reduced with great facility, the one to nitrous or hyponitrous acid and the other to chlorous or hypochlorous acid; and having been reduced they are just as easily re-oxidised. It is exceedingly probable that by this means they act as carriers between the lead and the electrolytic oxygen without being themselves permanently altered. Unfortunately, this instability of constitution has an attendant disadvantage, because a continuous reduction goes on at the negative electrodes, and the composition of the electrolyte is constantly altering; and this can hardly occur without more or less affecting the reactions at the positives.

It need scarcely be said that, considering how little is really known about the nature of the various reactions that go on during formation, the best electrolytes to employ in practice have been arrived at by actual experience and not upon any theoretical grounds. An unlimited number of solutions—not only acid, but neutral and alkaline—can be prepared in which some sort of a continuous production of peroxide will take place, but in almost every process worked on a large scale the nitrogen acids or salts play a part at one stage or another;

and, although it may be merely a coincidence, these acids comply in an exceptional degree with the three conditions just now enumerated. Whatever the reason, their use enables a layer of peroxide to be prepared, which, for intimacy and firmness of contact with the support can only be equalled, so far as the Author's experience goes, by a true Planté formation; and this is the first and most essential requirement. The oxidisation appears to eat into or corrode the metal, whereas with the majority of solutions the action takes place with such uniformity that the surface of the lead remains perfectly smooth, and the peroxide can get no proper grip upon it.

The most usual forming bath is a solution of sulphuric acid of specific gravity something between 1.050 and 1.150, to which is added some nitrate or nitrite of soda or potash—the salts of soda are generally given the preference because its sulphate is considerably more soluble than that of potash. It might be thought that a precisely similar result must ensue if free nitric acid were used in the first place, instead of decomposing one of its salts with the excess of sulphuric acid also present, but under the former condition it is extremely difficult to obtain a satisfactory formation; and this affords a striking example of the complexity of the causes which go to make up a successful process.*

The addition of nitrates is apt to give a somewhat unmanageable and irregular formation, owing to the liability of the nitric acid to attack the lead by local action with reduction to lower oxides of nitrogen, irrespective of the forming current, and the oxidisation then outruns the peroxidising effect; and this is one of the reasons why nitrites often have the preference. Either salt may give off copious red fumes when first added to the forming bath before the current is switched on, but should not do so afterwards to any extent.

All the nitrogen compounds in the electrolyte tend to become reduced to ammonia at the negative electrodes, but

* When an alkaline salt is employed, some acid sulphate is formed in the electrolyte, so that, in addition to the $\overset{+}{\text{S}}\overset{+}{\text{O}}_4$ ions, $\overset{+}{\text{H}}\overset{+}{\text{S}}\text{O}_4$ ions will also be present. This may have something to do with the difference in results and be the beginning of an explanation, but the alkaline ions liberated at the negative electrodes must also influence the rate and degree of reduction of the nitrogen acids which goes on there.

how fast and how far this change proceeds is a matter of circumstances. With a low-current density at the negatives it may go on extremely slowly and incompletely; with a high density nearly everything may be converted into ammonia in a comparatively short time, but the ultimate result depends on many other conditions besides the current rate. The point is one of very considerable importance, because it largely affects the degree to which the composition of the electrolyte varies during a formation, and the treatment necessary to free the positives from all traces of injurious compounds at the finish. It is possible that after a certain time, and especially if the current rate is increased, the positives may automatically seal themselves off in the same solution in which they have been formed, and only need thorough washing to fit them for use; but in any case it is far safer, and, in spite of the extra cost involved, the more general practice, to set them up again in a bath of dilute sulphuric acid only (except for ammonia left over from previous batches) and charge until every trace of nitrogen acids is eliminated from the plates and the electrolyte. This treatment has the further advantage that no attempt need then be made to promote a rapid reducing action during the formation proper; but, on the contrary, the endeavour will be to maintain those conditions which yield the most satisfactory production of peroxide. For the same reason it is often better to add the attacking salt in small portions at intervals during the formation rather than the whole amount at the commencement.

No formation can be considered commercial if the electrolyte has to be thrown away after once using; the cost of material and of handling then becomes far too heavy. On the other hand, the reduction to ammonia and the supply of fresh oxidising material can only be kept as low as possible and never entirely avoided, so there must always be a limit to the number of formations that can be performed in the same solution; for eventually it becomes choked with sulphates of soda and ammonia, which may impair its efficiency and will crystallise out all over the electrodes. Besides, even supposing the composition of the forming bath remains approximately the same for any one formation, it will not do so throughout the series, and the character of the attack will

vary somewhat with each from first to last. In general, it will be found that the first one or two formations in a new electrolyte do not give such good results as those following, and it is in every way preferable, therefore, to only remove and renew a portion of the electrolyte after each formation; or if it is not practicable to always do this, an entirely new one should, at any rate, be set up as seldom as possible. Analysis is not so much aid in adjusting the electrolyte as might be expected; the components are too complex and the essential conditions not known. Nitric, nitrous, hyponitrous, sulphuric, persulphuric acids, and soda and ammonia are usually all present. As soon as ammonia appears in the electrolyte it may form new ionic combinations by reacting with the nitrogen acids, and it is not at all unlikely that sulphuric acid combines with the latter to some extent to produce compounds such as nitrosyl sulphate. Hydroxylamine will hardly be formed so long as nitrous acid remains unreduced, but the Author has detected its presence on one or two occasions.

So far, nothing definite has been said as to the precise proportions in which a forming solution should be made up or the exact current rates to be used, and this for the very good reason that nothing definite can be said. In the first place, each of these conditions is altogether dependent upon the other, and both are largely affected by any number of third causes, such as the nature of the surface and the design of the electrodes to be formed; the distance away of the dummy negatives, and their relative superficial area; the temperature of the electrolyte, its relative quantity, and therefore the size of the forming tanks. A successful formation is the result of an extremely delicate adjustment between the whole of them, and can only be worked out on the spot where it is to be used and with the precise electrodes to which it is to be applied. Moreover, not one but several such adjustments can usually be made. For instance, with a small quantity of oxidising agent in the electrolyte and a low-current rate, a slow formation requiring several days for its completion will perhaps be arrived at; but by strengthening the solution, increasing the current rate, and raising the temperature of the cell, it may be possible to push the process through in a few hours.

However widely formations may differ in regard to the means and materials employed, they must all be ultimately judged by the cost and reliability of the process and the quality of the electrodes produced. The cost depends in the main upon three items: The cost of handling the electrodes, the cost of the electrolyte, and the cost of the forming current. A true Planté formation is undoubtedly the ideal one as regards handling expenses. The plates have simply to be set up in the forming tanks and removed when finished, for they do not even require washing, the electrolyte consisting of dilute sulphuric acid only. A quick formation, also comprising two handlings of the electrodes, plus a thorough washing, is possible but unusual, as they are generally set up a second time in a finishing bath of dilute sulphuric acid. This latter treatment may be merely a precautionary measure, but more often it is an essential part of the process, completing the peroxidisation of the active material and sealing off the electrode. If the forming solution is so constituted as purposely only to attack and oxidise the plates, practically the whole of the peroxidising being reserved till the finishing bath, the handling involved is not thereby increased; but there are other methods of oxidising by a preliminary treatment which greatly add to the labour charges. For instance, in the well-known Epstein formation, the plates are oxidised by a process of boiling in very dilute nitric acid and drying in air, which necessitates several handlings before the electrolytic treatment begins; and the latter is not simpler or less expensive than most others.

As regards the cost of the various solutions required for a formation, the true Planté process again takes the first place. The dilute acid lasts indefinitely, except for such as is removed with the electrodes or lost by gassing; and nothing else is needed. The materials of which an ordinary quick-forming electrolyte is composed are certainly not expensive in themselves, but if they had to be entirely renewed with each batch of plates their amounts and the labour of handling them would often be quite sufficient to add very seriously to the cost; as it is, the item is sometimes a pretty considerable one. It has, of course, to include the forming, finishing and any other electrolytes; also any solutions

employed in a preliminary treatment of the electrodes, and all washing liquids, for the latter are by no means negligible if weak acid or distilled water is used.

The Author has formed plates with a total current expenditure in ampere-hours of about four times the output that could then be obtained from them, and that result appears to him to be not far off the limit of what is theoretically possible—that is to say, the maximum ampere-hour efficiency of a formation process is about 25 per cent. The methods usually employed do not, however, yield nearly so good a result, and current equivalent to 10 to 20 times the output has to be expended, thus reducing the formation efficiency as low as 5 to 10 per cent. Apart from losses due to the shedding of loose peroxide, which can seldom be altogether avoided, this wasted energy is, no doubt, chiefly accounted for by the large amount of oxygen gas evolved, although some may be utilised in re-oxidising the compounds which undergo reduction at the negatives. In most formations the current has to be strong enough to maintain a vigorous gassing at the positives throughout the formation, or a satisfactory result will not be obtained; and, even where it is found possible to work just on or below the gassing point for some time, this state of affairs cannot be continued in the finishing tanks or towards the end of the process, when it is necessary to seal off the electrodes and eliminate all traces of the forming acids from them.

Even when electrical power can be very cheaply provided, the cost of the current is usually the most expensive part of a formation, and it is here that the true Planté process appears at a disadvantage, for its ampere-hour efficiency must always be very low. As the plates increase in capacity, the relative expenditure of current in discharging and recharging grows rapidly, until a practically prohibitive limit is reached. Some current might be saved by giving longer rests on open circuit, but then the time occupied would be out of all reason. As it is, the length of the process is one of its drawbacks, for it necessitates a large capital outlay in forming plant and electrodes undergoing formation, and a large area in which to carry on operations. The Tudor Accumulator Co. put the time occupied in forming their electrodes at about six weeks,

continuous night and day working; but it must have required a large amount of preliminary investigation, probably spread over years, to bring the process to that pitch of perfection.

The quality of the electrodes is, in the first place, dependent on the quality of the peroxide and its adherence to the support. Peroxide differs very much in appearance according to the process by which it is produced. A true Planté formation yields a highly crystalline, clear, brown peroxide, such as may be seen covering the surfaces of all positive lead supports—unless of antimonious lead—that have been in use for some time. Quick-formations often afford a darker shade, varying from a chocolate colour to puce or an almost dead black. The differences between the various kinds are not so marked when dry, though some seem to be broken up into much finer crystals than others; and, by itself, colour does not appear to have any special relation to quality, except in the case of an unhealthy-looking muddy-brown peroxide, which no doubt contains a considerable amount of sulphate—and perhaps other more dangerous salts—and indicates that the formation is defective.

The molecular structure of the peroxide is, however, all important. When it is obtained in the form of a dark impalpable powder like a paint, having no cohesion either within itself or to the support, it is evidently useless. Another variety which is dense and brittle is equally valueless but much more deceptive. In this instance the electrodes may be apparently well filled with a good crystalline active material, and yet when tested may have hardly any capacity. On examination it will be found that the peroxide has come bodily away from the support, and is simply lying loosely packed in the grooves or spaces provided for it: no doubt because, as it grew and expanded, its grip on the metal was too slight to stretch that at the same time, and so they had to part company. For this reason the moderate growth of an electrode during formation is generally a good sign; excessive growth, unless brought about by over-formation, indicates weakness somewhere—either bad design or defective material; but no growth at all shows merely nominal contact between the support and the active material.

Although readily recognised, it is somewhat difficult to describe the nature of a well-formed active material, except as the absence of those defects just referred to. It is a firmly adherent layer of porous-looking peroxide of uniform colour and texture throughout, and it should have no admixture of white or grey material either on its surface or underneath. In grooved electrodes the layers of peroxide very often expand and draw away from the support in a number of places but retain their contact at intermediate points, and the grooves look as if they had been filled with strips of corrugated peroxide. This characteristic appearance may be observed with the best formations, and does not seem to be accompanied by any diminution in the capabilities of the plates.

One of the most important factors, that must never be neglected in estimating the quality of the electrodes, is their electrical and mechanical durability. Sometimes, after the first few discharges, their output will rapidly decrease, either down to some point at which it remains fairly constant or until it is practically gone altogether. This invariably means that a part or the whole of the active material has become loosened from the support, although if it comes away in pieces and not in powder, and if the electrodes are of the usual grooved types, there may at first be very little actual shedding of peroxide to indicate it outwardly. A trouble of this kind is usually found out at the end of the formation if the electrodes are then subjected to a vigorous gassing by passing a heavy current through them, as that soon fetches away all peroxide not in thorough contact with the support. Incidentally, this is one of the advantages of such a treatment. It is much better to face the difficulty at that stage than to nurse the electrodes through the formation and have to deal with it afterwards, for if they will not stand a few overcharges when put to work they are of little use.

A more insidious danger, which in this case threatens the mechanical durability of the electrodes, is a continuation of the conversion of the support into active material, owing to its still containing remnants of the forming acids. The difficulty of removing these, and knowing when they have been removed, is one of the most serious drawbacks of so

many quick formations, and places them at a disadvantage as compared with the true Planté process, where nothing of the sort is possible. Many of the oxidised compounds obtained during a formation peroxidise just as readily as litharge or minium, and if the active material can be produced through their medium only, all is well, for they will then be entirely decomposed by the end of the process and their component acids returned to the electrolyte. There they can often be converted into something less harmful, as when nitrogen acids are reduced to ammonia or chlorine acids are oxidised to perchlorates; but, in any event, the electrodes may always be thoroughly freed from them by careful washing after removal from the tanks. There must, however, be other lead compounds, also containing the forming acids, which offer far more resistance to electrolytic attack, and once they appear in the electrodes they are not afterwards eliminated by ordinary treatment. Whether they are sub-salts, or too basic, or not sufficiently hydrated, or too heavily sulphated, or what may be the cause of their behaviour is not known, nor the conditions which give rise to or best avoid them. Their presence can only be ascertained by a chemical examination of the active material and the support, or, more practically, by putting the electrodes to work and observing how they go on. In bad cases they may be rotted through in the course of a few weeks, practically the whole of the metal being converted into a partially peroxidised grey-brown mass, and the electrode then breaks up. Considering how unlikely it is that anything beyond mere traces of the corroding agents are at play, the rapidity and thoroughness with which the attack can proceed is very remarkable. Usually the action is less virulent and more prolonged, and if the electrodes are of a fairly solid type, such as are used for stationary work, their failure arises from the indirect disruptive effects of the over-formation, perhaps before even the thinnest and most exposed parts of the support have been really destroyed. As the peroxide increases in quantity, packing more and more tightly into the interstices and getting a deeper hold on the surface of the metal, the plate is subjected to an increasing strain which is never perfectly uniform in every direction, and so it buckles or bulges. If the support is very rigid it may be ruptured in

places or the active material forced out sideways in its efforts to find room for itself, but when the plate is of good soft metal and thoroughly sub-divided it generally grows considerably before any actual fracture occurs. Even if the action is so slow as to require a couple of years to reach a climax, it is, of course, quite sufficient to render the plates unmarketable, or, if unwittingly used, to involve heavy expenses for their renewal.

With regard to the reliability of a formation process, little can be said, except to point out the extreme importance of obtaining it. A reliable process is one which can be depended on to give, time after time, the same results as regards the output and durability of the electrodes. Absolute uniformity is perhaps impossible, but the limits of variation should be small. It is very difficult to ensure this state of affairs; to know when it has been realised; to find out any departure from it before much mischief has been done; and, having found it out, to supply the proper remedy. The only course is to strictly adhere in every detail to a procedure that has once proved successful, but at the same time to ascertain as far as possible the precise effect of every variation from it, so as to take advantage of any real improvement that can be introduced and to be prepared to deal with any deterioration of results that may occur.

When forming electrodes packed with a number of separate pieces of metal, it is very necessary for each one to have an initially good and equal contact with the support, otherwise the current will be very irregularly distributed amongst them; some must then be over-formed, some under-formed, and it will be almost impossible to seal off properly and eliminate all traces of the forming agents. The extreme case of this type of construction is furnished by supports packed with metallic lead very finely divided by some mechanical means—so-called “lead dust” electrodes. These are more akin—except perhaps for the quality of their active material—to plates pasted with lead oxides. They are generally formed by the true Planté process, for, owing to the large surface of metal exposed to electrolytic action, the peroxidisation proceeds rapidly and the whole of the metal is soon attacked.

Pasted Active Material.

Monoxide of lead or litharge, and minium or red lead, are the raw materials employed for the preparation of this class of active materials. Monoxide of lead, PbO , is produced commercially by two different methods. It is obtained as a kind of by-product in certain processes connected with the refining of lead, but more especially in its cupellation. In this case the oxide is formed at a temperature above its fusing point, is run off into iron pots, and when it has solidified the mass is turned out and left to cool. During this process it gradually breaks up into crystalline flakes and the product is termed "flake litharge."

The second method consists in exposing molten lead in a furnace to the action of air for the express purpose of preparing its oxide. The temperature is not raised sufficiently to melt the oxide, and the lead is ultimately converted into a dross consisting of monoxide in admixture with particles of metal which have only been imperfectly attacked. It is then ground and washed by levigation to remove the latter, and again put in the furnace to dry; the resultant powder used to be called "massicot," but the term "litharge," formerly applied to the fused oxide only, is now used more or less indifferently to describe all kinds of monoxide, however prepared, and it will be employed here in this broader sense.

Litharge varies very considerably in colour, from a lemon-yellow to an orange-buff, not only with its mode of manufacture, but also according to the degree of fineness to which it has been ground. Its colour does not, as a rule, bear much relation to its purity, but if it is of a pale dingy yellow hue this generally indicates the presence of some proportion of finely divided metallic lead due to imperfect washing after oxidisation. Neither of the two processes of manufacture just referred to can be said to produce a purer oxide than the other. In the first case the quality of the litharge depends chiefly on carefulness of manipulation; in the second case, the purity of the massicot is simply a matter of the purity of the lead used. Small quantities of impurities in the raw active materials are not perhaps so disastrous as when they occur in the support itself; but, all the same, lead oxides

containing more than traces of either copper or antimony should be avoided, for unless removed during formation they will eventually find their way to the negative active material and set up local action there.

Red lead or minium is prepared by the further oxidisation of massicot. After the oxide has been levigated and put back into the furnace it is subjected to a carefully regulated heat—considerably less than that required for its own production—for from 24 to 48 hours, according to the colour required and other circumstances. Although minium is supposed to have the composition Pb_3O_4 , it often does not contain much more oxygen than may be represented by Pb_4O_5 , but, on the other hand, it is said that very occasionally it may approximate to Pb_2O_3 . Corresponding partly, perhaps, to the varying percentages of oxygen, but also to the fineness of its subdivision, it exhibits slight differences of colour between a dull red, scarlet and orange-red, but they are not nearly so pronounced as in the case of litharge.

When powdered litharge is mixed to a paste, not necessarily with dilute sulphuric acid, but with a solution of almost any acid, alkali, salt or soluble organic substance, it eventually sets to a hard dry porous mass. There can be little doubt that, however diverse the reactions between the oxide and the substances in solution, the setting action is always due to hydration or chemical combination with the water itself, for precisely the same result is obtained if pure water only is employed; and the effects observed present a close analogy to the hardening of lime or plaster of paris under similar conditions.

From a practical point of view, however, the nature and amount of the substances in solution is of great importance, for they appear to combine with the oxide to form indefinite basic lead compounds, some of which hydrate and harden not only more rapidly but more perfectly than others. In the case of a dilute solution of a caustic alkali, such as potassic or sodic hydrate, the action is somewhat different. Indeed, the alkali prevents the paste from setting, and simply dissolves some of the oxide to form a soluble plumbite; but the action of the carbonic acid in the air slowly decomposes this compound into an alkaline carbonate and a basic lead carbonate,

and then hardening takes place. This reaction was made use of by FitzGerald in one of his processes for preparing lithanode. It is quite probable that the carbonic acid of the air may often be a factor in the proper setting of a litharge paste, although in a less marked way than in the case just mentioned. At any rate, considerable quantities of carbon dioxide are generally absorbed during drying and given off again when the electrodes are placed in a solution of sulphuric acid.

Most of the solutions that will set litharge have no such effect on red lead. When, for instance, it is mixed to a stiff paste with water, the mass dries without any cohesion between its particles, and tumbles to pieces on the slightest touch or shock. Dilute sulphuric acid decomposes red lead, as may be seen by the change of colour from red to brown, most probably converting it into a compound of sulphate and peroxide of lead; and then it will harden gradually, much as a litharge paste does under similar conditions, except that no carbon dioxide is absorbed while drying.

Red lead was the oxide employed by Faure in the preparation of both positive and negative active materials. A little later it was realised that by substituting litharge at the negative, a given quantity of spongy lead could be obtained with a less expenditure of forming current, and so the use of litharge for the negative paste and minium for the positive paste became the recognised practice. Red lead is now very seldom employed for the negatives, but, on the other hand, litharge is frequently given the preference for the positives because it appears to furnish a harder and more durable active material. Others, again, pin their faith to mixtures of litharge and minium in various proportions, and use either a similar or different mixture at both electrodes. Where experience shows that litharge does yield an improved result its adoption may be well worth the extra expenditure in forming current.

Dilute sulphuric acid is the fluid generally employed for mixing the paste, whether of litharge or red lead; in the latter case, indeed, there is very little practical alternative, for, although a few other strong acids decompose red lead, there are distinct objections to their use. A fairly satisfactory active material may be produced with most strengths of acid,

but the details of manipulation in the pasting, seasoning or formation will not be the same for all of them, and some are much easier to work than others. Taking everything into consideration, the choice generally falls on some specific gravity between 1.100 and 1.200, which can only be more precisely determined by direct experiments with oxides of the same quality as are actually going to be employed. "Quality" in this connection does not refer to the percentage of impurity present, but to something more subtle. It is very remarkable how widely the results that can be obtained from a pasted active material vary, both as regards output and durability, with different samples of lead oxides. Anyone may convince themselves that this is so by procuring a few pounds of litharge, here and there at random, and trying. Uniformity of results can only be achieved by keeping as much as possible to the same brand; and even that must be frequently checked by setting up formed plates and testing them.

Mixing the paste is apparently a simple operation, but one that requires considerable care. The solution should be added in small portions at a time, and each one be thoroughly mixed in. In this way the oxide will take up a considerable quantity, and still appear as dry and loose as at first, but beyond a certain point it suddenly passes to a rather thin paste, which does not yield a satisfactory active material. To obtain a paste of the proper consistency, the amount of solution must be regulated so as just to stop short of this stage, and then, if the oxide is thoroughly worked up with the spatula or trowel used for mixing, it will gradually cohere into a stiff, greasy-feeling mass. As a rule, the better the paste the longer is the time required for mixing and the greater the muscular effort involved, and this, unfortunately, gives rise to a temptation to ease the labour by using a slight excess of solution or perhaps somewhat modifying its strength. Even when the process is carried out carefully and conscientiously some men make much better pasters than others; there appears to be a knack in the manner of mixing the paste and filling it into the electrodes which is necessary to procure the best results.

Abroad, mixing and pasting machines have been largely introduced and although these may eliminate the personal

equation and reduce the cost of manufacture, they probably have their drawbacks. No sooner is a paste mixed than it begins slowly to set, and the sooner therefore it is in position on the support, the harder and stronger will it ultimately be. Where large quantities at a time are mixed in a machine the portions last used can hardly be so good as the first, and in this respect the ordinary practice of taking a weighed quantity of oxide, only sufficient for a few electrodes, mixing in a measured amount of solution and pasting straight away, must have an advantage.

What may be termed the standard method of preparing active material from a paste of lead oxides and dilute sulphuric acid applied while moist to the support, is capable of numerous modifications in every direction. The dry oxides can be filled into the support and then moistened, either by spraying or simply by immersing the electrode in the solution, after having first wrapped it temporarily in some porous fabric. In many cases the pasted electrode is subjected to considerable pressure in a press. This has the double effect of consolidating the paste and forcing it into thorough contact with the support, and also of squeezing out all the superfluous moisture, which is removed by absorbent sheets placed on either side. In the opposite direction, increased porosity is provided for by mixing various substances with the oxides and dissolving them out later on by simple solution or electrolytic action. Finely powdered carbon is one of the most favoured materials of the latter kind, magnesium sulphate of the former; but very many others have been used. Finally, the mixing fluid comes in for endless variation. Other substances, such as various sulphates, glycerine or acetic acid are added to the sulphuric acid or used by themselves. In all these matters, results are the only possible test of utility, and so far as can be ascertained, no two of the modified processes run on quite the same lines, so it is questionable whether any one of them is pre-eminently superior to the others. Just as with the formation processes, so here the introduction of other substances besides sulphuric acid should be avoided unless distinctly advantageous, for it is difficult to entirely eliminate them afterwards and almost impossible to say what may be the ultimate effects of even the most apparently

harmless compounds. In many cases it will add to the cost of manufacture, because the forming acid may have to be changed at more or less frequent intervals, and the formed electrodes subjected to a more or less thorough washing according to the nature and amount of the foreign materials that are present.

After the paste has been applied to the electrodes it must be allowed to harden thoroughly before they go into the forming tanks, otherwise the active material will probably be deficient in coherence and durability. All processes or treatment between the pasting and the forming are commonly spoken of as "seasoning." This may consist in merely leaving the plates stacked with access of air, for days or weeks together, for it is surprising how long they sometimes are in attaining to their maximum hardness; but, if desired, the result can be hastened by placing them in a moderately-heated drying chamber. Although a good paste should set hard, hardness is by itself no certain indication that the resultant active material will possess the same quality. Occasionally the very hardest pastes will be entirely disintegrated within a few minutes of their being placed in the dilute acid electrolyte preparatory to forming. The cause is difficult to assign, but appears to have some connection with the paste becoming too hot when first mixed, and it may possibly be due to an unstable superhydration of the litharge.

A preliminary treatment in weak sulphuric acid often forms a regular part of the seasoning, for besides weeding out faulty plates it is supposed to harden the remainder. The plates are dipped in the acid for a few minutes, then removed and allowed to dry, and this may perhaps be repeated two or three times at intervals. It has already been mentioned that unformed litharge pastes which have been exposed to the air for any length of time give off considerable quantities of carbon dioxide when first placed in the acid, and, provided the solution is fairly weak, they should be able to endure this evolution of gas without showing any signs of disintegration. If they do commence to break up, the gas is probably not the prime cause, but merely accentuates a weakness already existent, as indicated above. Anyway, electrodes that have to be carefully nursed through their first immersion in acid—

unless there is some special reason for an excessive generation of gas, such as the use of a carbonate in pasting or hardening—seldom prove durable in use.

If a pasted material cracks as it dries, then shrinkage is going on, and it will probably also draw away from the support in places. Under such conditions satisfactory results cannot be obtained, and the fault must be found and remedied—most likely the acid used for mixing was too weak. A good material will expand slightly during seasoning and so be forced into thorough contact with the support. If a paste sets with a dense close grained surface of different texture to the interior, it has been mixed too wet or the surplus moisture has not been properly removed afterwards. This is one of the most frequent causes of blistering, scaling, and surface sulphation in comparatively new cells.

Formation.

The electrolytic reduction or peroxidisation of litharge requires the expenditure of 109 ampere-hours per pound or 240 ampere-hours per kilo, apart from the current that is wasted in the evolution of hydrogen or oxygen or in other incidental reactions. The fact that the litharge is partly sulphated or combined with other acid radicles during pasting or afterwards only affects the E.M.F. at which the formation will proceed. Minium or red lead can be peroxidised with 71 ampere-hours per pound or 157 ampere-hours per kilo, but its reduction—a procedure seldom adopted nowadays—would need twice these quantities, namely, 142 and 314 ampere-hours respectively. These figures are based on the assumption that its composition is Pb_3O_4 , but, as it often varies somewhat from this formula, they can only be regarded as approximations.

When forming pasted electrodes, the reduction or peroxidisation of the raw material does not take place more or less simultaneously throughout the mass, as is the case when formed plates are recharged, but commences at the surface of contact with the support and gradually spreads outwards. The rate at which the action can proceed is proportional therefore to the area of this contact surface, but it is always limited by the specific susceptibility of the unformed material

to electrolytic attack, and this varies very considerably, according to its composition and the method of its preparation. If too large a current is employed the formation may be retarded rather than accelerated, because the electrolyte will be displaced from proper contact with the active surfaces by the gas generated, and, in its endeavour to escape, the unformed material may be loosened or broken up and so permanently removed from the circuit. On the other hand, an unnecessarily slow formation is not desirable, as it allows the last portions of the unformed material to become so heavily sulphated by the prolonged action of the acid electrolyte, that they can only be attacked with great difficulty and a considerable waste of energy.

It is evident, then, that no hard-and-fast rule can be laid down as to the proper forming current, either in terms of the electrodes or the amount of material they contain, but each case must be decided on its merits and be checked by experiment. As a rough guide it may be said that, if the plates are thin, the support and active material well subdivided, and a considerable surface of the support in direct contact with the free electrolyte, they may be formed at 3 to 4 amperes per pound of oxide. If, on the contrary, the plates are thick, and the active material is present in large undivided masses which cover nearly all or the whole of the support, 1 to 2 amperes per pound of oxide will be quite sufficient. According to the rate, the time occupied in forming will range from about 30 to 120 hours for litharge pastes, and will be about one-fourth to one-third less for red lead pastes. Grid electrodes of a thickness, and with recesses of a size such as are generally adopted in standard makes, come somewhere between the extreme figures just mentioned. Their formation will usually occupy from 40 to 60 hours, at a current of 2 to 3 amperes per pound of oxide.

The absence of gas is, of course, a sure sign that a formation is not yet completed, but the evolution of gas may merely indicate that the current is larger than can be properly absorbed. Caution must be exercised in assuming that the formation is finished even when the electrodes gas freely at a low current, and their surfaces appear to be thoroughly reduced or peroxidised. The electrolytic action is always inclined to

proceed more rapidly at the lines of junction between the support, the raw active material and the free electrolyte than elsewhere, and to spread from thence right over their exposed surfaces before the whole of the interior has been attacked; and when this has come about it is almost impossible to avoid superficial gassing during the remainder of the formation. To definitely ascertain how long a formation at a given rate must be continued it is safest, in the first place, to open up one or two electrodes after various amounts of current have passed through them and examine their active material.

Under favourable conditions the ampere-hour expenditure during formation need but slightly exceed the theoretical figures. The chief enemy of efficiency is the unequal distribution of the forming current, and this tendency is accentuated by strong currents, dense raw material and thick electrodes. In certain cases, when the raw material has little porosity, or where large pieces whose area of contact with the support is small have to be dealt with, they are superficially peroxidised as soon as possible in order to provide a larger surface from which the action can spread inwards. Sometimes this is effected by a special preliminary treatment, sometimes by pressing sheets of perforated lead against the electrodes while forming, sometimes merely by a high current rate. Under these circumstances great efficiency of formation can hardly be expected, for gas will be given off throughout the process.

With many types of electrodes better and more efficient results may be obtained by grading the current rate to correspond to alterations of the area or disposition of the surface over which electrolytic action is taking place, rather than by maintaining it of uniform strength throughout. For instance, the initial forming current for electrodes containing rod or sheet supports entirely covered with raw material must be kept very low, but as the formation proceeds the surface of contact between formed and unformed material approaches nearer and nearer to the free surface of the electrolyte, while with rod supports the area of the surface also increases rapidly, and so the current may be raised in proportion. For electrodes, such as those of the grid type, in which the support comes to the surface in numerous places—

and this is the more general case—the above conditions are reversed. The area of active surface tends to decrease in amount, and, by reason of the rapid surface formation, is gradually forced inwards; and in all such cases it is advantageous to lower the current towards the end of the process.

There is no intrinsic objection to unformed positive and negative electrodes being opposed to each other in the tanks and formed at the same time, and the method presents obvious advantages with regard to economy of space and electrical energy; nevertheless it is generally found preferable to form them separately, against dummy positives or negatives as the case may be, so that each may receive the treatment best suited to them in respect of current strength, time of formation, and composition of the electrolyte. The combined method is most applicable when the electrodes are identical as regards design and the quantity and quality of the active material they contain, but this does not often happen.

It is sometimes found that, when special pasting solutions have been used, the electrodes cannot be satisfactorily formed both as positives and negatives. In such cases they are either all peroxidised, and the negatives obtained by reversal, or all reduced and the positives reversed. This procedure adds considerably to the cost of formation, and should, if possible, be avoided; it is not necessary nor advantageous under ordinary conditions of manufacture.

The forming electrolyte is generally dilute sulphuric acid of 1.100 to 1.200 specific gravity. During the early stages of formation, acid is frequently absorbed by the electrodes, but is returned again at the end, together with the acid used when pasting, and so the density of the solution falls at first, but finishes stronger than it began. The electrolyte has, therefore, to be frequently broken down, probably after each formation, for, if it is allowed to get too strong, the raw active material may become so heavily sulphated that the acid can only be again eliminated with considerable difficulty. Care must also be taken that the small quantities of impurity that pass from the active material into the electrolyte at each formation do not accumulate there or on the dummy plates, and prove a source of trouble. For this reason it may be

advisable to change the entire electrolyte occasionally, and to thoroughly cleanse the dummies.

Lead Chloride as Raw Active Material.

Cast lead chloride is the only compound of lead, other than its oxides, which serves as the basis for the preparation of active material on any considerable scale. By itself, the pure chloride casts short and brittle; but in admixture with something under 10 per cent. of zinc chloride it yields a tough substance, from which a negative active material, consisting of fibrous crystals of lead, very coherent and of high porosity, can be obtained. Positive active material cannot be prepared by the direct formation of the chloride, but only by reversing negatives. In this process the crystalline structure entirely vanishes, and, whether this be the cause or not, positive electrodes produced in this way have generally proved unsatisfactory, and they are but little used: their active material has a large output but little durability.

About the good qualities of the negative active material there can be no doubt. Some details of its manufacture, as practised by the Chloride Electrical Storage Company, will be found in Chapter X. A good many processes are involved, and, apart from the cost, which is considerable, the greatest care is necessary at every stage if a proper result is to be ensured. Pure chlorides of lead and zinc in solid admixture may be perfectly—although somewhat slowly—reduced by zinc in a strong solution of zinc chloride; but, if they also contain any oxy-chlorides, their complete reduction then becomes a matter of great difficulty, even under the most protracted treatment. In consequence, the electrodes may very easily pass into use still containing both zinc and chlorine, and, as these gradually work out of the active material, they are quite likely to bring about its disruption. Unfortunately, the normal chlorides have a great affinity for oxygen, and oxy-chlorides are very liable to be formed, hence the difficulty. Experience has proved that, by the exercise of due precautions, these troubles can be avoided; but anyone starting *ab initio* to make use of lead chloride as raw active material must certainly come to grief in the direction indicated unless the utmost caution is exercised.

Electrolyte.

It need scarcely be said that great attention must be paid to the purity of the acid used for pasting and forming and also for filling the cells after they leave the factory. The first stage in the manufacture of sulphuric acid is the preparation of sulphur dioxide, SO_2 , by roasting either sulphur or sulphide of iron. In trade terms, the former yields "sulphur" or "brimstone" acid, the latter "pyrites" acid. Unless very carefully purified, pyrites acid almost invariably contains traces of arsenic, iron and other metallic impurities, and for this reason sulphur acid should always be employed for battery work.

A more dangerous contamination, to which both kinds are equally liable, is the retention of minute quantities of the oxides of nitrogen, which are used for converting the sulphur dioxide into trioxide. Hydrochloric acid is occasionally found to be present, but there is no excuse for its getting into sulphuric acid in the course of manufacture; this can only be a result of carelessness. If in dilute acid, it probably came there with impure water employed for breaking down, and this is frequently the source from which traces of nitrites are also derived. Distilled water should always be used for diluting the pure acid. Often on doing so a fine white or brown-white precipitate of lead sulphate or sulphide is thrown down. The lead has been dissolved from the pans in which the acid is concentrated and is not harmful. If, however, the acid is mixed with hard water the precipitate may merely be due to the lime that is present. An acid which affords a pink colouration at any stage of charge or discharge, when used as an electrolyte, in all probability contains traces of manganese and its use should be discontinued.

The complete examination and analysis of the acid requires scarcely less judgment and skill than is necessary for the other raw materials. An approximate idea as to its quality may, however, be formed by means of a few simple tests carefully made, and these are given at the end of the next chapter.

CHAPTER VIII.

THE TREATMENT AND TESTING OF LEAD CELLS.

The right treatment of lead cells may be said to consist in preventing their active materials from becoming abnormally sulphated, or, as it is often more shortly termed in practice, "sulphated"; for, by avoiding the conditions which favour or bring about this state of affairs, other troubles, such as the undue corrosion of the positive supports or the normal sulphation of the active materials on open circuit, will also be guarded against.

The distinction between normal and abnormal sulphation will here be regarded as one of degree merely, without considering any further and more fundamental differences of chemical constitution that perhaps exist. So long as the percentage of lead sulphate produced in any part of the active material does not exceed a rather vaguely defined limit, it is normal sulphation; but wherever the sulphate is in excess, the active material is there abnormally sulphated.

Although there must be a small range of composition where the properties of the two states merge and pass from one to the other, the difference between them is otherwise clearly marked, and probably results from a very big difference of specific resistances. Normally sulphated active material can be desulphated electrolytically—that is to say, it can be recharged—without any trouble; but when abnormally sulphated it is either not attacked at all, or only with extreme difficulty and very slowly. It has, in fact, almost ceased to form part of the electrolytic circuit, and is, therefore, no longer "active." This in itself constitutes a very definite objection to abnormal sulphation taking place, for evidently material

that cannot be recharged cannot be discharged again, and the output of the cell is proportionately diminished; but it is also dangerous on account of the undue increase of bulk by which it always appears to be accompanied.

The first result is to choke up the pores of the active material, diminishing its porosity and giving rise to conditions which tend to aggravate the original trouble, and, unless proper treatment is resorted to, rapidly increase the area affected; but after a certain stage the mischief becomes more pronounced, and the active material is disintegrated or the support damaged.

If abnormal sulphation is merely excessive sulphation, or a direct result therefrom, it must invariably be preceded by normal sulphation, and discharged cells must be the most readily affected, charged cells the most resistant. Whether the assumption is correct or not, there can be no doubt as to the truth of the conclusions to which it leads, for they have been thoroughly established, and all the generally accepted rules for the treatment and management of cells are based upon them.

Strictly speaking, the discharge does not itself involve abnormal sulphation, because when any portion of the active materials reaches the verge of this condition its increased resistance automatically shunts it out of the circuit; or, if the whole is affected, the P.D. of the cell falls rapidly to zero and the output ceases; but the further the cell is discharged, the nearer will it be brought to the dividing line.

Treatment on Discharge.

The P.D. should always be taken as the gauge of the safe discharge limit, irrespective of what output the battery has already given or is still capable of yielding; for although in practice other causes besides sulphation are largely responsible for the fall of voltage, it probably never drops below 1.8 volts without the production of a dangerous percentage of sulphate at some part or another of the active materials. When the rates of discharge are high, the loss of E.M.F. by internal resistance and weakening of the electrolyte in immediate contact with the active materials becomes so pronounced that the output is often allowed to proceed to a lower P.D.; but,

for reasons to be given directly, this latitude should be very sparingly exercised.

Experience has shown that a battery lasts much better if never discharged below 1·85 rather than 1·80 volts per cell, and better still if 1·90 volts is the limit; but the latter figure means too much initial expense to be generally adopted. Probably a fair compromise between output and durability, or between prime cost and maintenance, is a P.D. varying from 1·85 volts for low-discharge rates to 1·80 volts for high-discharge rates. Lower figures than these are best avoided, unless a large output for weight is the prime consideration.

It is somewhat difficult to determine what are the precise causes which operate to convert normal into abnormal sulphation; but it seems most likely that anything capable of setting up local action between the electrolyte and either of the active materials will effect this result. In all probability only an extremely small amount of extra sulphation is necessary when an active material is already normally sulphated to its full extent, and a quite insignificant agent may bring it about. Local action may arise in various ways. Doubtless one of the most usual is through the traces of foreign substances which are often to be found in the active materials of the electrolyte. Copper, iron, manganese, arsenic, hydrochloric acid and nitric acid—every one, in fact, of the most frequent impurities—are all capable of maintaining local action for an indefinite period without being themselves destroyed; and so their effect may be out of all proportion to their quantity. Most of them will pass to and fro between the positive and negative, and undergo alternate oxidisation and reduction; but in the case of copper it remains deposited in the negative active material.

The appropriate tests for the detection of the various impurities are given further on. Sometimes one or more of them will be present in a battery from the start, owing to carelessness or ignorance on the part of the manufacturer, or they may find their way in with after-additions of water or acid. It is always advisable to use distilled water for "topping-up" cells. If this is not available, and hard water has to be employed, it should preferably be boiled first and the sediment allowed to settle, so as to free it from as much

lime as possible. It is not certain that lime is injurious in a cell, but its presence is better avoided. If necessity compels recourse to water containing traces of nitrites or chlorides, it should be added just before charging, and the battery should receive an extra thorough charge. This will reduce the one to ammonia or oxidise the other to perchloric acid, in which forms they are comparatively harmless. A possible source of metallic impurity is the salts produced by the corrosion of unprotected brass connecting bolts and nuts, or the ironwork of stands and other battery-room fittings, and when these are used due precautions must be taken to prevent this from happening.

High rates of discharge are credited with being a most potent cause of the abnormal sulphation and rapid deterioration of electrodes, and in general this view is justified; nevertheless, traction regulator batteries which are constantly discharging at the one-hour rate, or still faster, have been found to endure remarkably well. In the latter case, however, the cells are discharged at the one-hour rate for, say, on an average, a minute only at a time, and with one-minute recharges between each discharge; whereas, under ordinary conditions of treatment, the battery is fully discharged in one hour and recharged perhaps in the next hour, or perhaps much later. The conclusion appears to be that a high rate of discharge is only dangerous when sufficiently prolonged to over-discharge some portions of the active materials and exhaust the electrolyte in others; the moral is that the sting of a discharge at high rates is in its tail, and that, in spite of the increase of output gained thereby, it is a questionable policy to allow it to proceed to a lower P.D. limit than is found advisable for low rates. This is especially so in tramway traction with accumulators, where the limitations of space accentuate the polarisation effects; and it is then often preferred not to attempt to realise anything like the full output of the cells, but to recharge them at frequent intervals, while their discharge P.D. is still high.

Treatment on Recharge.

The surest means of preventing abnormal sulphation, from whatever cause, is always to recharge a battery the moment it has finished discharging, and to keep it fully charged between

the discharges. During the earlier stages of the recharge the current is chiefly absorbed by the normally sulphated active material most favourably situated with regard to the support or the free electrolyte, and only as these parts become desulphated, and their counter E.M.F. rises owing to the increase of gaseous polarisation, will it be diverted to the outlying portions or to any abnormally sulphated material of high specific resistance.

For this reason the benefits to be derived from prompt recharge will not be experienced if the current is discontinued merely because the cells are commencing to gas or because a few more ampere-hours have been put in than were taken out. By so doing it may probably happen that just the active material which most needs desulphation will be left practically untouched and ready to become abnormally sulphated by a little local action with the hydrogen peroxide or other highly-oxidised products almost sure to be present in the electrolyte after a recharge.

If the previous discharge has been at a very high rate, or continued to a very low P.D. limit, or spread over a long period with intervals of rest in between, or if, as often happens, it has not been found possible to follow on with the recharge immediately, then the necessity for ensuring a thorough recharge becomes all the more urgent, as in all these cases some of the active material will certainly offer a more obstinate resistance to desulphation than the remainder.

If proper attention is paid to a battery, and suitable records are kept, the most certain indication, not only of the completion of a recharge but of the general condition of the cells at any period of their life, is afforded by the specific gravity of their electrolyte. To begin with, it is necessary that the preliminary charge on first setting up, and also the few following charges, should each be continued until the strength of acid ceases to rise any further, and in this way it will soon be worked up to a maximum which may be taken to correspond to the entirely desulphated state of the active materials, and serves as a standard for future reference. So long as the specific gravity at the end of every further recharge can be brought back to this figure nothing could be better. In many cases, however, especially if the electrodes contain large

percentages of active material or are badly designed, it may be found that to accomplish this requires the expenditure of an excessive amount of energy, and the strength of acid is gradually allowed to drop back to a point at which it can be maintained with a fair efficiency of working. This means that some portion of the active material becomes permanently sulphated, and, although not an ideal condition of affairs, may not be of much consequence if the reduction of acid strength is slight; but if this does not suffice, either efficiency must be sacrificed or the sulphation may pass beyond control and the electrodes be ruined.

Normally, a battery may be kept in good order by always charging until the P.D. per cell attains to some value which depends upon the type and construction of cell, strength of electrolyte, rate of charging and other circumstances, and can only be precisely determined by observation. Information as to the best limit of charging voltage for any particular make should be obtained from its manufacturers. It may be anything from 2·5 to 3·0 volts, but is generally something between 2·6 and 2·7 volts. It is often assumed that the charging plant need only be capable of providing 2·5 volts per cell as a maximum, but this is seldom sufficient even with charges at slow rates. Sometimes that or a still lower figure is adopted with the idea of ensuring the best possible results as regards efficiency, but the practice is an unsound one. As often as not it defeats its own object in the long run, for presently prolonged charges will be required to overcome obstinate sulphation; and there is always a risk of some of the cells being irretrievably depreciated and the life of the whole battery shortened.

In no case should a final P.D. be accepted as the guide to the necessary amount of charging current unless it is found to be consistent with a maintenance of the electrolyte at its proper strength. Still less to be relied upon by itself is the plan of charging a battery until the ampere-hours put through it exceed those of discharge by some fixed percentage, which may be anything from 5 to 25 per cent. The method has no flexibility, and either the battery will at times be uselessly over-charged or, what is more likely, the charge will not always be sufficient to keep it properly free from sulphate.

Charge and discharge meters adjusted to read too low in the one direction by the desired percentage are sometimes introduced into the battery circuit and the charge continued until the index returns to zero, but the deficiencies of this arrangement are now better realised than they used to be and it is not so often employed.

From what has just been said, it should be quite clear that maximum electrical efficiency and maximum durability are ordinarily incompatible. If durability is given the first place the efficiency will then depend upon the nature of the cells, and should be a fair one if they are well designed and suited to their work; but if efficiency is too much striven after, it is more than likely neither will eventually be realised.

Seeing that full and frequent charging is so essential to the proper maintenance of lead cells, it appears strange that for some years this very treatment should have been considered the surest way of ruining a battery, and users were warned to stop the current the moment a free evolution of gas could be observed, or even earlier.

This state of affairs was due to the very exaggerated ideas entertained at that time as to the rate at which the metallic lead of the positive supports could be oxidised and destroyed either by the direct action of the current or by local action with the adjacent layer of active material on open circuit. In this respect, Gladstone and Tribe's early researches proved somewhat misleading, for they apparently revealed an amount of oxidation which, if it actually went on in working cells, would render them of little practical use. All oxygen that could not be accounted for at the positive when charging was naturally thought to have combined with the lead, whereas it is now known that it goes to form superoxidised products with the electrolyte. Although no doubt the mistake largely arose from this cause, some of their other results still seem inexplicable, unless the lead supports or the lead oxides used in pasting them were impure and in a condition to be very readily attacked.

Even at the present day it is sometimes believed that the oxidation of the positive supports proceeds somewhat in proportion to the amount of overcharging which they receive; but, as a matter of fact, when once the surfaces of a pure lead

anode in an electrolyte of dilute sulphuric acid are peroxidised and gassing they are most thoroughly protected from any further action all the while the current is maintained, and it may be continued for an indefinite period without more than the merest film of peroxide being produced. On open circuit local action does occur, but here again, as Drake and Gorham were the first to assert, as soon as a layer of peroxide of sufficient density and thickness has been formed it is itself the real protection for the support, and any further attack only proceeds extremely slowly unless the peroxide is sulphated and broken up. Over-discharging, not over-charging, is, therefore, the real promotor of the peroxidisation of the positive supports.

Such dangers as do pertain to overcharging depend upon the rate rather than its amount. Heavy currents effect a considerable concentration of acid in the pores of the positive active material, and after gassing has set in, are very favourable to the formation of an excessive quantity of peroxidised compounds in the electrolyte. This is objectionable, because they conduce to local action with the active materials and loss of output when on open circuit; probably also to abnormal sulphation in discharged cells. The more obvious drawbacks of high rates at the end of the charge arise, however, from the purely mechanical action of the evolved gases. In moderation this is distinctly beneficial, for it tends to keep the electrolyte stirred up and of uniform density and to free the active materials from superficial scale and sulphate; but when they are given off at too great a rate their disruptive effects become very appreciable, and they may cause a rapid disintegration of the active material if its coherence is not of the best. Different electrodes will endure very different rates of gassing with comparative impunity according to their type and design, but the maximum current will always be far less than can be put through them with perfect safety so long as it is entirely absorbed in desulphating the active materials.

There is, indeed, at the commencement and during the earlier stages of the recharge, a minimum limit below which the current cannot be satisfactorily reduced, in spite of the fact that the lower the rate the better the results so far as a uniform distribution of the current throughout the active

materials and an equalisation of acid strength within their pores are concerned. Unless an E.M.F. sufficient to produce a certain degree of polarisation is applied to the cell, the desulphation of the active materials only proceeds very partially, and can never be thoroughly completed; for if the initial current is too low, a battery may be charged almost indefinitely without its E.M.F. rising in a normal manner or much gassing setting in; while under a continuance of this treatment it will gradually deteriorate in output and evidences of abnormal sulphation presently manifest themselves.

All this points to graduated charging rates being the best for cells rather than the usual practise of charging at constant current. The "normal charging rate" of the maker's catalogues is some such rate as will effect a full recharge in from eight to fifteen hours. It is, on the one hand, a little above the permissible minimum for an effective initial charging current, while, on the other hand, it can be continued right up to the end without causing a violent generation of gas; nevertheless it may, with advantage, be tailed off somewhat when gassing commences. The "maximum charging rate" is usually about double the normal rate, and here the advisability of moderating the current towards the finish is very certain. If, as happens occasionally, a charging plant is hardly equal to its work, a special effort should be made to maintain the normal current, or more, for the first hour or so while the E.M.F. is low, even if it has to be diminished afterwards.

The extreme example of graduated charging rates is afforded by constant potential charging, a method which has already been discussed in Chap. IV., p. 180. It still remains a moot point whether or not the enormous initial currents and the excessive concentration of acid they must produce are injurious to the life of the electrodes, but it is in all probability a case of a right principle being carried too far. That the current is automatically varying throughout is all to the good, but the fault lies with the whole recharge being completed in too short a time. To do this, unless absolutely compelled, is to adopt a course which lowers efficiency without adding anything to the durability. The better plan is a graduated charging current spread over as long a period and at

as low an average rate as would be employed if the charge were at constant current, for this is the one means by which maximum efficiency may be attained without sacrificing durability.

Apart from other considerations, charging at constant potential is not practicable in its rigid simplicity, because the size of the generating plant has to be out of all proportion to the storage effected; but in a modified form it is found very useful in power stations where a large number of small units, such as tram or motor car batteries, are constantly being recharged at rapid rates. By means of boosters, current is provided at two, three or four different voltages, and the discharged battery is first connected to the lowest of them, then, when the current has fallen to a predetermined figure, to the next highest, and so on through the series. By this arrangement the extremely heavy initial currents, which overtax the generators, and perhaps damage the cells, are avoided, while the final stage is carried through a little more briskly than at constant potential.

In all cases of charging at one or more fixed voltages the only certain test of the completion of the recharge is afforded by the specific gravity of the electrolyte returning to its proper value just as in constant current charging. The P.D. necessary to effect this must be determined on its merits, as also must the final current limit. As the bulk of the output is restored in the first part of the recharge—if the same voltage is maintained throughout, as much as 80 to 90 per cent. of the total output may be returned in the first half—there is a considerable temptation to cut short the later stages, but in view of the strong acid concentrated in the active materials by the high initial currents it is important not to do so.

Treatment on Open Circuit.

In theory, it should be possible to leave fully charged cells on open circuit indefinitely without any sulphation of the active materials and consequent loss of output; in practice, there is almost sure to be some amount of local action, and perhaps electrical leakage as well, so they require to be occasionally recharged although no useful output has been furnished in the interim. As a rough working guide it is usually recommended to do this from once a fortnight to once a month, but

the best treatment is often more satisfactorily decided on its merits by observing the behaviour of the cells on the recharge, for, in this respect, not only different makes but different batteries of the same make may differ very largely.

A battery should never be left so long that a free evolution of gas from both positives and negatives cannot be produced by two or three hours charging at the normal rate. As a rule the positives commence to gas almost immediately the current passes, but the negatives, where most of the local action goes on, may not do so for many hours, and, unless care is exercised to see that the multitude of fine bubbles which impart the milky appearance to the electrolyte are being evolved from the negatives, it is very easy for the charge to be prematurely stopped. It is, however, most undesirable that the electrolyte should become surcharged with a large quantity of peroxidised products, as these will sulphate and discharge the negative active material during the next spell on open circuit; so, after the positives gas, the current should be kept very low just as when completing an ordinary recharge. For the same reason it is advisable that the solution used in cells which have to remain idle for long periods together should not exceed a density of 1.150 to 1.170 when at its maximum strength. Further, it is sometimes advocated that on each occasion the bulk of the working acid should be withdrawn after thoroughly charging and be replaced by water or extremely dilute acid, but this treatment is hardly worth the trouble involved unless the circumstances are very exceptional or the ordinary electrolyte unusually strong.

When negatives run down rapidly on open circuit and lag very much behind the positives on recharging it is most probable that they are experiencing an excessive amount of local action, due to the presence of traces of copper, antimony or other impurities in the spongy lead. In this event there will be a more or less rapid liberation of hydrogen gas at their surfaces all the while they are at rest. The cause of the trouble can only be eradicated by elaborate treatment, but, provided the battery is well looked after and frequently charged, it will not do much harm; if, however, care is not taken, the negatives may soon begin to show symptoms of abnormal sulphation.

If, after standing idle for a while, neither the positives nor negatives gas until they have received a considerable amount of current, it points to leakage, and the insulation of the battery and of the external circuit must be looked to. When cells have to go for a long time without recharging, each one should be uncoupled from the remainder—assuming they have clamped connections—so as to break up the E.M.F. into the smallest possible units. If this cannot be done, the whole battery should, at any rate, be cut off from as much of the external circuit as possible by disconnecting all the supply leads.

There may be another and more serious reason for the running down of positives on open circuit, especially if the negatives are not similarly affected, and that is local action going on between the active material and its support. This should not occur to any practical extent if all the materials in the cell are pure, and it is generally a result of defective manufacture or of impurities introduced with the electrolyte. Very often a trouble of this kind is beyond cure, and the positives are soon ruined by corrosion and over-formation. In some cases prolonged charges at heavy rates, followed by a change of the electrolyte, may help to seal off the plates and do good, but the proper treatment can only be decided after expert examination, and perhaps an analysis of electrodes and electrolyte to ascertain the destructive agent.

Treatment of Sulphated Cells.

If lead cells are correctly designed, carefully manufactured and properly treated, in accordance with the principles just discussed, it is easy to keep them in order, but once they have been allowed to go wrong it becomes a far more difficult matter to restore them to a healthy state; in fact, unless the defect is of the slightest or is dealt with at an early stage, they will seldom return to as good a condition as at first—that is to say, over-sulphation of the active materials may be averted more readily than desulphation can be effected; and its results are hardly capable of reversal at all.

The remedy is the same as the preventative—charging, and plenty of it. The current first reacts on any normally sulphated active material that may be present, and when this is

accomplished the electrodes begin to gas and the E.M.F. of the cell rises as usual. The remaining material is now attacked in two different ways. Such of it as is not too heavily sulphated still continues to undergo electrolytic reduction or peroxidisation; and is very slowly and with a great waste of energy brought back to the conductive state. This accounts for the increase of output that can certainly be brought about in sulphated cells by prolonged charging. But such as is entirely sulphated and has assumed the characteristic white appearance of non-conductive PbSO_4 cannot be rendered "active" by any amount of charging, but it may be dislodged by the mechanical action of the gas bubbles, and gradually falls to the bottom of the cell in flakes and powder, thus clearing the choked-up surfaces of the active material and giving an increased access of electrolyte to its pores.

Great virtues have been claimed by Barber-Starkey, Salomons, Preece and others for an electrolyte containing a small quantity of soda—1oz. to 2oz. of sodium hydrate, carbonate or sulphate per gallon—in addition to its usual acid. Not only is it supposed to hasten and make more perfect the recovery of badly-sulphated cells, but it is sometimes said to retard sulphation in the first instance. Battery makers, however, seldom recommend its employment, and the opinion of many who have tried it is that it makes no difference whatever (this has been the Author's experience), nor are the specific examples of its success which have been put forward such as to carry much conviction. It would appear, therefore, that its effects, if any, are only felt under certain conditions, which yet remain to be investigated.

An electrolyte which is sometimes found useful for the prolonged charging of badly-sulphated negatives is simply a weak solution of sulphuric acid, about 1.050 specific gravity; but as it involves changing and then replacing the working liquid of ordinary strength, it is not often resorted to in practice.

The best general indication that all goes well with a battery is furnished by an uniformity of behaviour amongst its cells. Both on discharge and recharge their P.D.s and the specific gravity of their electrolytes should rise and fall together

and between the same limits; gassing should also commence almost simultaneously in each one. Directly the readings begin to get irregular, it clearly shows that the work is proving too much for the battery and is overstraining the weaker cells—for, even with the most careful manufacture, they may differ very appreciably amongst themselves. The discrepancies are most apparent towards the end of discharge and recharge, as it is then that slight differences of condition produce the largest effect upon the P.D. As the stronger cells approach the limiting voltage, some of those whose specific gravity is lowest will be found to be dropping considerably below it in the one case and not rising to it in the other.

If the severe usage is exceptional, a few extra long charges at a low rate should equalise the battery again; but if these do not effect the purpose, or if the trouble recommences when they are discontinued, the treatment must be modified as speedily as possible, or the weaker cells will soon go from bad to worse. Indeed, they do not need to lag much behind for their E.M.F.s to be temporarily reversed towards the end of the discharge, and than that nothing more conducive to abnormal sulphation could occur. Most probably the battery is being under-charged or over-discharged. If the former, the final P.D. of recharge should be raised, or, what usually comes to the same thing, the percentage of ampere-hours put back in excess of those taken out increased. If the latter, the discharge should be stopped at a higher P.D. limit, or the rate of discharge reduced; or it may be that too long intervals elapse between the discharge and recharge. Should the discharge be at fault, increased charging will help to minimise its effects, but it cannot altogether neutralise them.

Although the depreciation of batteries is generally a result of their being worked too hard, it sometimes arises from their not having enough to do—as, for instance, when the discharge is intermittent or at a very low rate and spread over days or weeks, or when the battery stands absolutely idle for weeks and months together. In such cases the mischief can be wrought by an amount of local action quite insignificant and negligible under ordinary circumstances, but whose culminative effects are very considerable when it is able to continue uninterrupted for such long periods.

Treatment of Short-Circuited Cells.

When a battery is allowed to get thoroughly out of condition by sustained overwork or underwork or neglect, the mechanical effects due to the expansion of abnormally sulphated material soon begin to manifest themselves and produce shunt or short circuits, either by the supports buckling and touching one another or by the loosened active material falling away and lodging between them. If the contact is of low resistance, the cell very quickly discharges itself and becomes practically dead, yielding next to no E.M.F. on open circuit, but perhaps a small P.D. on charge and a still smaller one in the reverse direction to the rest of the battery on discharge. The specific gravity of its electrolyte also drops to an extremely low value and remains there. More usually the short circuit is not so complete and the symptoms not so pronounced. The cell does not gas as soon as the others on recharge, and if the current is maintained for the purpose of levelling it up, the P.D., and very likely the density also, cannot be forced as high; while on open circuit or discharge it runs itself down more quickly, so that on the next recharge it is found to be lagging as much behind as ever, and no amount of charging or other modification of treatment will permanently restore the cell unless the cause of the trouble is first removed.

Flakes or pieces of active material can generally be dislodged from between the plates with a thin strip of wood or ebonite; but if the electrodes have buckled into contact, or if the sediment has collected at the bottom of the cell until it bridges their lower edges together, they will have to be taken out to straighten them or to clean the containing box. Large central station cells are, however, sometimes provided with a wash-out plug, through which the mud can be cleared without disturbing the plates.

Within a short time of their removal from the electrolyte, charged negative electrodes become hot and dry owing to the rapid oxidation of the spongy lead, and on again placing in the acid, sulphation by local action at once commences, much as when new cells are first set up. For this reason they should be exposed to the action of the air as little as possible. If neither

positives nor negatives require attention, the complete section can be immediately transferred to another box arranged ready to receive it, and the electrolyte be then poured in ; or the separate plates can be stored in acid while the old box is being cleaned. If only the positives need be seen to—and this is the most likely—they can generally be withdrawn by themselves and the negatives left in the liquid meanwhile.

Single positives should be straightened between boards so as to distribute the pressure, rather than by direct blows with a mallet ; and if they are badly distorted it will even then have to be done gradually and carefully, else they may fracture or the bulk of the active material come away. When the damaged plate or plates are burned up into a section, boards of suitable thickness should be slipped between each one, and two others placed on the outside. An increasing pressure can now be applied by some arrangement of long bolts passing through holes in the outer boards, or in cross-pieces which slip over the boards, with nuts for tightening up. A very good clamp can often be rigged up, especially in emergencies, with a pair of belt stretchers.

It may be found impossible to start with spacing pieces of the full thickness on account of the risk of breaking the joints on to the main connecting bar. Thinner boards must then be used at first and be replaced by others after the worst of the curvature has been taken out.

If the whole or the best part of the cells have to be dismounted for cleaning the boxes or attending to the electrodes, the battery should be charged as soon as possible after setting up again. The amount of the charge will depend upon the previous state of the plates and the length of time they have been kept out of the electrolyte. If they were very heavily sulphated or the exposure to the air prolonged, it may need to be continued almost as long as a first charge ; but, if they were fully charged to start with and expeditiously handled, a few hours may suffice to cause a free evolution of gas from both positives and negatives and to bring the density of the electrolyte up to its maximum value.

Even in batteries which are well looked after and properly treated, trouble may from time to time be experienced with individual cells, arising possibly from some defect in their

manufacture, or from the bending of a plate in careless mounting so that it touches its neighbour, or from purely casual short-circuiting by detached active material. In such cases it hardly pays and may be exceedingly inconvenient to charge the entire battery for the sake of one or two cells, nor is it to be recommended if these require a very prolonged charge. Where the connections from cell to cell are made with bolts and nuts or other detachable couplings, the faulty cell should receive the normal charge with the rest of the battery, but be cut out of circuit on each discharge—by disconnecting one terminal lug and bridging a wire from the other to the free lug of the adjacent cell—until it comes up level with the remainder and can again take its share of the work. If it is necessary to make the charge of the cell more continuous, both its terminals may be disconnected after the ordinary recharge of the battery is completed, and then re-connected with bridge-pieces, so as to bring it into circuit in the reverse direction. All the discharge current of the battery will then be utilised as charging current in this cell; but not more than one or so can thus be treated at the same time, otherwise the total P.D. of the battery will be too much lowered, even with all the regulator cells in circuit.

In central stations or other installations where the cells are permanently lead-burned to common bars, it becomes impracticable to disconnect single cells from the circuit every time they require extra charging or to be relieved from some of the discharge load. It is now the practice in the larger plants to provide a special booster or "milking" dynamo to meet the difficulty. This supplies current at only a few volts pressure, and is directly connected to the bars of any cell that requires to be overcharged until the plates gas so thoroughly that the electrolyte assumes a milky appearance—hence the name. To facilitate its use special lead-covered conductors are often run from the booster down all the rows of cells, and are tapped off at any required point with short connecting pieces. Not only can any cell be charged when the rest of the battery is on open circuit or discharging, but the booster can take up its work during discharge so as to enable it to be disconnected for repairs without breaking the main circuit. The latter object may also be attained by

joining a liquid resistance consisting of lead plates in dilute sulphuric acid across the cell bars.

An alternative to a low voltage dynamo is two or more spare cells so arranged that they can be switched in at one end of the battery when they themselves require charging or to be used as additional regulator cells, but can be entirely disconnected from it when employed in nursing up any other cell to which they have to be coupled through a variable resistance. Although such cells are in every way inferior to a booster machine, it is almost imperative that one or the other should be available if a battery with lead-burned connections is to be properly maintained.

Regulator cells are often the first to go wrong in a battery, for, although they get less discharge than the others, they are very apt to be cut out of the circuit on recharge directly they begin to gas and before their P.D. has risen sufficiently; nor are there any records by which the relative amounts of output and input can be checked. It may often be noticed that the one or two extreme regulators, which perhaps seldom come into circuit and then only for a short time, are in better condition than the rest of the cells, while the remaining regulators are distinctly the worst. The readiest plan for specially watching these is to always keep a hydrometer in each one and see that the specific gravity of the electrolyte returns to its full value on each recharge.

Commercial Testing.

The testing of accumulators comes under two categories: laboratory tests to ascertain their qualities and capabilities for the purposes of the manufacturer, the inventor or the scientific investigator; and the tests of batteries in commercial use to see whether they are in good condition and to detect the cause of any departure therefrom at the earliest moment. The general nature of these latter tests has already been indicated in this chapter but it still remains to consider in somewhat more detail how and when they must be made to be most effective.

Isolated readings from a battery or its component cells may reveal glaring defects, but the fuller information which enables the trouble to be prevented rather than cured can

only be obtained by comparison with similar preceding readings, and a consideration of the whole antecedent treatment. This is why properly tabulated records are insisted upon for all batteries maintained by contract, and they should always be kept if the longest life and lowest cost of upkeep is to be attained.

The data recorded may be more or less elaborate according to the size and importance of the battery, the conditions of working, the appliances provided, and whether it is entrusted to skilled hands or otherwise; but it should always comprise two portions—a day-to-day log of the working of the battery, and tests, at intervals, of each of the cells.

Under the first head must be entered up the date of every recharge, its time of commencement and finish, and the rate. If the current is reduced towards the end, an average rate should be booked, and if it varies very much it may be advisable to note the maximum rate as well. The four following P.D.s may all be recorded with advantage:—

On open circuit just before recharging begins.

Just before the charge is stopped.

Shortly after the discharge has commenced.

Just before the discharge finishes.

The current flowing when these tests are made is often included in some other part of the records, and does not very much matter unless it varies largely from time to time or is at a very high rate. What is of more importance is to note the number of cells to which the P.D. refers, or else to make a practice of always reading off from the same number, preferably with all the regulator cells out of circuit.

The output of a battery is, as a rule, at too irregular or intermittent a rate to measure except by a recording instrument or an ampere-hour meter, and one or both of these should be introduced into the discharge circuit of all large batteries. In central stations it is becoming the practice to employ recording ammeters which will indicate the charge and discharge currents on opposite sides of a central zero line. From the diagrams the output and input can be calculated and entered up much more accurately than by attempting to average a number of detached ammeter readings, and

the amount and duration of the various rates of current can be seen at a glance.

Opinions differ as to how often the specific gravity and P.D. readings of individual cells should be made. If they are required after every charge and discharge their frequency will probably defeat their purpose, for it is rather a wearisome business going properly through a large number of cells, and the sheets may even get filled in without that trouble, or at any rate the measurements be made in a very perfunctory manner. It is so much easier to pass rapidly from cell to cell with a hydrometer and a cell-tester, just dipping the former in and out and resting the contact-bar lightly across the lugs, and, unless a very bad fault has cropped up, assuming that the figure is the one expected and the same as yesterday's. It takes time to let the hydrometer come properly to rest; see that it is clear of the electrodes or the side of the box, and then read off the exact line where the stem cuts the surface of the electrolyte. Also, the voltmeter connections generally need a little moving about before they scrape away the skin of sulphate on the lead and give a P.D. unaffected by variable resistances at the points of contact.

Weekly readings are the more usual practice. The densities of the electrolyte should first be obtained on open circuit before the commencement of a discharge, and then the P.D.s shortly after it has begun, special attention being paid to any cells whose specific gravities are irregular. If any voltage is decidedly below the others it points to a bad short circuit. A second set of tests are again made shortly before the end of the discharge. Cells which were up to the mark or nearly so in the earlier tests but now read much below the average—especially the P.D. which may be in the reverse direction—are probably slightly shorted or else not equal to their work.

The important indications as to the state of a battery which are to be derived from the behaviour of the electrolyte in the cells are liable to be very readily confused and misinterpreted unless certain precautions are observed in its management.

If the same strength of acid is put into all the cells on first setting up, and their electrodes are of uniform make, the electrolyte should, after the first charging, approximate very

closely to the same density throughout. Often, however, considerable differences will manifest themselves as the charging proceeds, owing to faulty or irregular manufacture. In those cells where the strength rises above the prescribed limit some of the solution should be drawn off from time to time and be replaced by distilled water. Those cells, however, in which it is too weak should not be interfered with until after the first few discharges. Then, if it is quite certain that it will not rise any further by charging, it may be levelled up, either by drawing off the electrolyte and at once replacing it by a ready-prepared mixture of the desired strength, or by adding acid of a specific gravity not exceeding 1.400. Undiluted sulphuric acid should never be used for this purpose. In this way all the electrolytes can be ultimately brought to the same figure and to stand about the same height in the cells, usually from $\frac{1}{2}$ in. to 1 in. above the level of the electrodes.

No further acid should now be added to the cells under ordinary circumstances, but all loss of electrolyte by evaporation and gassing should be made up by the addition of water sufficiently often to prevent the tops of the electrodes from being exposed, and in sufficient quantity to maintain the original level. In the course of time there will be a slight weakening of acid in all the cells, owing to some being carried away with the spray and some entering into permanent combination with the active materials and going to form the sulphated sediment which gradually collects at the bottom of the boxes. To make up this waste a little acid may at intervals be added to every cell, putting the same amount of the same strength into each. A note should be made on the records of all additions either of water or acid, otherwise it may be difficult to afterwards account for discrepancies in consecutive readings of the densities.

Working under these conditions it becomes possible to refer all irregularities of the electrolyte in special cells, or unusual variation in the whole battery, to some abnormal cause which has to be discovered. Instead of doing this the mistake is sometimes made of supposing that the defective specific gravity is itself the trouble, and more acid is added to bring it back to its ordinary value, thereby only covering up the fault and possibly aggravating it. In

reality, change of density has, within reasonable limits, little effect on the working of the cell, and its importance lies solely in its being a symptom of the true malady. Only after the cells have been put to rights, and the strength of their electrolytes restored as much as possible by charging, should any further acid be added to compensate for irreversible sulphation and to equalise them with the others.

When tests to arrive at some idea of the condition of a set of cells have to be made on the spot and without the aid of records, P.D. readings should be taken on discharge, as it is then that the effects of contacts between the plates are most marked. On open circuit or recharge partially short-circuited cells may easily be overlooked, for their readings are often almost the same as the others, but directly a discharge is started their P.D.s drop rapidly and somewhat in proportion to the magnitude of the fault.

Apart from the direct positive tests, lead cells afford many slight visible indications by which anyone experienced in dealing with them can form a very good idea of their state. The chief of these is the colour and appearance of the active materials. Fully charged and unsulphated peroxide ranges in colour from an almost velvety black to a deep chocolate, and becomes a lighter red-brown when discharged; but it must be remembered that different makes of electrodes vary a good deal in regard to the exact shade of colour they present under similar conditions. It is, however, possible for any of them to be most obstinately sulphated and yet show little or no traces of white sulphate.

Laboratory Testing.

The practical laboratory testing of accumulators as distinct from purely theoretical investigations only involves measurements of P.D. and current, and these can all be made with a good dead-beat voltmeter of the "moving-coil" type and a reliable ammeter. Mirror galvanometers, potentiometers, condensers, and so forth are superfluities, except for purposes of calibration. Their one direct application is when attempting more accurately to disentangle internal resistance from polarisation than can be done with the commercial instruments; but the results, besides not being strictly correct even so

obtained, are of no practical use, for what really matters is internal resistance *plus* polarisation, and this is furnished by the ordinary P.D. curves of discharge and recharge. Indeed, a set of these curves taken at different rates provides the best possible general statement regarding all the vital qualities of a cell, and is more comprehensive in its scope than are the characteristic curves of a dynamo or the indicator diagrams of an engine in their respective spheres.

The real difficulty in testing cells consists in so arranging their treatment and contriving the conditions under which the measurements are taken that the figures obtained for output, efficiency and durability shall convey some true and definite information as to their actual and comparative merits. None of the three qualities just mentioned have a fixed value apart from treatment, and that may be so manipulated as to furnish the most misleading results. A failure to realise this fact has vitiated the work of some of the most careful and impartial experimentalists in the past, and it is still often unconsciously or deliberately taken advantage of by those with preconceived hopes or aims.

The causes which give rise to this state of affairs have been discussed in Chapter IV. under the headings of "Output" and "Efficiency," and when these are understood the lines on which it must be dealt with are readily discerned, and may be summed up in the following remarks.

Cells should be tested under as nearly as possible similar conditions of treatment to those they will have to endure in practice, according to the class of work for which they are intended. The treatment should be sustained for as long a period as possible, and the whole of the results during the time taken into account. Conclusions based on single or detached discharges and recharges are of little value.

It does not do to arrange matters so as to secure the best results, on the assumption that these may be reduced by various percentages to arrive at what may be expected under other working conditions. It often happens that the most promising cells deteriorate quickest and most thoroughly under a little indifferent usage, and prove vastly inferior to others which could not attain to so high a maximum at first.

The substitution of what may appear to be equivalent or even more arduous treatment in place of that actually to be encountered in practice is apt to prove misleading. Cells may be worked much harder in the laboratory, so far as the amount of discharging and recharging in a given time is concerned, than they will have to do in reality, but this does not determine their condition after the same number of discharges spread over a far longer period and with considerable intervals on open circuit.

At least two cells are necessary for any test, so as to check one another, and several more should preferably be employed, and an average taken of their behaviour.

Chemical Testing.

The chemical tests for the presence of the impurities usually to be found in the electrolyte, the raw active materials, or the metal of the supports are for the most part simple and sensitive, yet they require care in the making, else they may prove ineffective or misleading.

The Author has more than once seen a heavy precipitate of sparingly soluble sulphate of silver thrown down by adding a saturated solution of silver nitrate to a strong solution of sulphuric acid, and then cited in all good faith as a proof that the electrolyte was reeking with chlorides. Or, in looking for iron, strong acid, perhaps absolutely undiluted, is taken; a good dose of strong nitric acid is added, and then a saturated solution of ferrocyanide of potash. Such a mixture is capable of furnishing all the colours of the rainbow and of indicating the presence of iron derived from the ferrocyanide itself, quite irrespective of what the acid under examination may have contained. The fact is, the appropriate tests are often selected from some chemical text-book, and are carried out without any of the ordinary precautions as to strength of the solutions and other details that are taken as understood in a work of that sort; or it is not appreciated that, when applied to a solution containing a very large percentage of sulphuric acid, the results may be considerably modified.

In general, the various reagents required for testing may be prepared by diluting their cold saturated solutions with about 10 times their volume of water. To the solid substance,

roughly crushed if in lumps or large crystals, is added a quantity of distilled water not sufficient to dissolve the whole of it after standing for 24 hours, with occasional shaking ; or, if the solution is needed in a hurry, the water can be heated and allowed to cool, when it should re-deposit an excess of the dissolved salt. The clear liquid is then poured off from the residue and diluted. This is not a scientific method, but it dispenses with the necessity for scales and weights, or even measures, as the latter can be gauged by the eye with sufficient accuracy. Although the strength of the reagents may often be varied through wide limits without really interfering with the delicacy of the tests, yet it is preferable to maintain an approximate uniformity in this respect, as it facilitates the institution of a comparison between results obtained from different samples.

For "dilute acid" the pure concentrated acid should be mixed with 10 volumes of water.

Distilled water should invariably be employed for all testing operations. If tap or well water has to be resorted to, it must be borne in mind that it will almost certainly contain some chlorides, perhaps a little nitrite, and, more rarely, traces of iron.

The acids—sulphuric, hydrochloric and nitric—employed in connection with the various tests themselves require to be examined to see that they are free from impurities. This is best done by performing a dummy experiment—*i.e.*, omitting the substance to be tested—for each reaction in which they have to take part. Iron, copper, arsenic or nitrogen acids are frequently present in sulphuric acid ; iron or hydrochloric acid in nitric acid ; and arsenic in hydrochloric acid.

In most cases the figures for the sensitiveness of some of the reactions, which will be found in the following pages, fall considerably short of the extreme indication that can be observed in a solution known to contain the substance sought for, and are those which may be assumed to represent the inferior limit of their accuracy if ordinary care is taken.

Iron.

Iron responds differently or not at all to the same tests according to whether it is in the ferrous (less oxidised) or ferric

(more oxidised) state. The orthodox test is first to add a few drops of dilute nitric acid and boil the solution to convert any ferrous into ferric salt, and then a solution of ferrocyanide of potash. If iron is present a deep blue precipitate will be thrown down, or, in the case of traces only, a blue colour will appear, with perhaps a precipitate on standing. This answers all right for a considerable quantity of iron, but the nitric acid is apt, unless very sparingly used, to react with the ferrocyanide and produce a colouration on its own account. If, therefore, the indication of iron is slight, it is best to repeat the test without nitric acid, and should iron be present the colour will either appear at once or after shaking for a minute or two to bring the solution thoroughly in contact with the air. A direct test for iron in the ferrous condition is a solution of ferricyanide of potash, which produces the same blue compound as ferrocyanide does with a ferric salt; but, as traces of iron are seldom present in that form, and as the ferricyanide solution does not keep at all well and is very liable to give false indications, its use is not to be recommended.

A second test for ferric iron is a solution of sulphocyanide of potash or ammonia, with which it yields a blood-red colour. No indication is obtained with ferrous iron, so a preliminary boiling with a drop or two of dilute nitric acid may be necessary.

Both the ferrocyanide and the sulphocyanide reactions are very sensitive, and are not interfered with by an excess of sulphuric acid of the ordinary strength of an electrolyte. They will indicate one part of iron in considerably upwards of 250,000, but at their faintest the former imparts a green and the latter a pink tint only.

Copper.

An excess—*i.e.*, more than sufficient to neutralise the acid—of ammonia gives a deep blue colouration in the presence of copper, but as this test will not reveal much more than one part in 20,000 it is seldom of any use in battery work.

Ferrocyanide of potash is a most sensitive test for copper as well as for iron. It gives a red-brown precipitate, or with traces a colouration only. It will indicate one part

of copper in more than 100,000 of solution, but at its limit only shows a change from the lemon-yellow tint imparted by the ferrocyanide to one of a buff hue. It is sometimes advisable to increase the range of this test by evaporating some of the sulphuric acid to dryness, taking care that the dense fumes evolved are carried up a flue or into the open air. The residue is then dissolved up in a drop of dilute nitric acid and the ferrocyanide added to it in the basin.

A still more delicate test for copper is xanthate of potash (a compound produced by the reaction of carbon bisulphide with an alcoholic solution of potassic hydrate), which affords a brilliant yellow precipitate or a colouration only, according to the amount present. It is claimed to be capable of indicating one part of copper in nearly 1,000,000, and it will certainly detect one part in upwards of 500,000. The xanthate must be used in a considerably diluted solution, or it will be too much decomposed by strong solutions of sulphuric acid. In any event a faint opalescent cloudiness will probably be formed through this cause, but it should be of blue white tint without a tinge of yellow when held against a piece of white paper. In doubtful cases the colour should be compared with that of another test-tube containing acid of similar strength but known to be free from copper.

Manganese.

Traces of this metal are often to be met with in sulphuric acid, especially in that which also contains iron, and it is most probably the source of the pink colour which sometimes appears in the electrolyte. Provided no hydrochloric acid is present, an extremely delicate test is to add a little dilute nitric acid and some lead peroxide to the diluted sulphuric acid and boil the mixture. The most minute quantity of manganese will then show a pink colour; but it must be ascertained by a preliminary trial that it is not derived from the peroxide itself, for this frequently contains it as an impurity.

Arsenic.

Traces of arsenic in the form of arsenious acid are the most frequent of all impurities in commercial sulphuric acid. Marsh's test is considered the most delicate means of detecting

them. It consists in adding the suspected liquid to a flask in which the evolution of hydrogen, by the action of dilute sulphuric acid upon granulated zinc—both perfectly free from arsenic—is taking place. Any arsenic is precipitated upon the zinc and then evolved again as arsenuretted hydrogen, H_3As . The gas issuing from the delivery tube of the flask is lighted, and on holding a crucible lid, evaporating basin, or other piece of white porcelain in the flame, a brown or black metallic stain forms upon it should arsenic be present, but otherwise it remains quite clean.

The above test, although simple and only requiring appliances which are part of the equipment of every laboratory, is not one which can be carried out without them and at a moment's notice, and for this reason Reinsch's test is to be preferred. To a little of the diluted acid in a test-tube is added not less than one-tenth its volume of concentrated hydrochloric acid. An inch or so of thin copper wire is cleaned quite bright with glass-paper, rolled up small and dropped into the acid solution, which is then raised to boiling. If the copper becomes black or brown it indicates arsenic.

This test, though possibly not so delicate as Marsh's, is exceedingly sensitive, and a quantity of arsenic too small to respond to it can certainly be ignored. With the merest traces the copper turns a bronze-brown colour, as if very much oxidised, but the solution may need to be boiled for 10 to 15 minutes before this takes place. There are very few samples of commercial acid which will not tarnish the copper under this test, and even "chemically pure" acid often gives some slight indication of arsenic. It must not be forgotten that hydrochloric acid is itself very liable to contain arsenic, and has to be tested separately after diluting to about one-tenth. The copper should remain absolutely clean and bright.

Other metals, such as bismuth, silver, mercury and antimony, are also precipitated by copper from an hydrochloric acid solution, but none of them are likely to be present in new acid under ordinary conditions. Antimony might be contained in the electrolyte from a cell having supports of hard lead, but it would more likely have all been deposited in the negative active material.

Nitric and Nitrous Acids.

The ordinary test for these is afforded by their behaviour with a solution of a salt of iron. If undiluted sulphuric acid is under examination, a little is taken in a test-tube, mixed with about its own volume of water, allowed to cool thoroughly, and some ferrous sulphate solution then run carefully in on the top so that the two liquids do not mix. This is best done by means of a pipette or piece of glass tube drawn out to a point at one end. Should any nitrogen acids be present they are reduced by the ferrous sulphate (which is itself converted into ferric sulphate) to nitric oxide, and this, dissolving in a further portion of the solution, produces a ring of the characteristic deep brown colour at the plane of junction of the two liquids. If dilute acid or other solution has to be tested, then it must be mixed with its own volume of strong sulphuric acid, free from iron, and the same procedure followed as before.

As it soon oxidises in contact with the air, the ferrous sulphate solution is best prepared afresh each time it is required by dissolving a few crushed crystals in a little cold water in a test-tube. The solution should be strong but not fully saturated, or some of the salt will be re-precipitated in an opaque cloud where it comes in contact with the acid.

The foregoing test is not a very delicate one. It will hardly reveal more than one part of nitric acid in 5,000 to 10,000, and at the limit the test-tube will have to stand by for half-an-hour or so before the ring appears, and may have to be held against a sheet of white paper to show it up clearly. An acid which responded to this reaction would indeed be badly contaminated, and some other detector is necessary for the traces which are more often present and yet are too large to be allowed to pass unchallenged.

This is furnished by brucine. On adding a few specks of dry brucine or brucine sulphate to concentrated sulphuric acid diluted with about one-fifth its own volume of water, it will, if nitrogen acids are present in the most minute proportions, turn a crimson or pink, passing more or less rapidly to orange and yellow. Dilute acid must have several times its own volume of concentrated acid mixed with it before adding

the brucine, or the brucine may be dissolved in a little pure acid in a test-tube, and the liquid under examination then carefully run in on top so as to form a separate layer. The colouration appears at the plane of contact, possibly beginning with a purple, which passes to pink and yellow as before. The solution of brucine in acid will not keep its efficacy for long and must be freshly prepared at the time of use.

The ultimate transition to yellow takes place at once upon heating, and, therefore, to obtain the pink, which is the most sensitive and characteristic indicator, the acid should always be thoroughly cooled after its dilution and before adding the brucine. Even then the rate of change varies very considerably with slight differences in the conditions of the test.

It must be borne in mind that brucine is a poison, only somewhat less deadly in its effects than strychnine.

A still more delicate indicator for nitrogen acids is diphenylamine, which yields a magnificent blue when used in an exactly similar manner to brucine. Its solution in concentrated sulphuric acid, diluted with about one-fifth its volume of water, may, however, be kept ready for use. About as much as would cover a sixpence—as the doctors say—dissolved in 5 fluid ounces of concentrated acid and 1 fluid ounce of water is a useful quantity.

The sensitiveness of both the above tests is very great, responding readily to one part of nitric acid in 250,000 to 500,000 and upwards. Unfortunately, many other oxidising agents produce the same effects, and considerable circumspection is necessary, therefore, in using them. Diphenylamine is the most susceptible in this respect, and on that account brucine is sometimes to be preferred to it. New acid is not likely to contain anything besides nitrogen acids, except, perhaps, selenious acid in large quantity, which would give the reaction, but in acid which has been used as electrolyte in cells there is almost certain to be some amount of persulphuric acid and hydrogen peroxide, and very likely other compounds which will respond to the test.

Hydrochloric Acid.

A few drops of dilute solution of silver nitrate will indicate, by a faint opalescence due to the formation of insoluble silver

chloride, the presence of as little as one part of chlorine in 500,000. With larger quantities the precipitate is of a white curdy character. To avoid the possibility of silver sulphate being thrown down, the saturated nitrate solution should be diluted with 10 to 20 volumes of water, especially if the acid under test is not very much diluted. If it is not acid but water that is under examination a drop or two of dilute nitric acid should be added before the silver solution.

CHAPTER IX.

THE ERECTION, CONNECTING UP, AND REGULATION OF LEAD CELLS.

It is of first importance that batteries should be so arranged that each individual cell is easily accessible for the purpose of inspection, applying the routine tests, and, when necessary, removing the electrodes for cleaning, repair or renewal. Cells are almost invariably set up in rows on racks or stands; preferably in single rows with the top of the cell boxes about 3ft. from the ground, and a passage way on either side of them. Unfortunately, this plan requires more floor space than is always available, and a more compact arrangement frequently has to be adopted. Either the rows can be placed in two or even three tiers, one above the other; or, if the cells are not very wide—measuring width at right angles to the length of the row—two rows may be placed side by side; or both these methods of economising space may be employed in combination. Very often the stands are fixed all round the walls of the battery room, but this is not to be recommended, for it increases the difficulties of properly examining the cells, especially if they are more than one row deep or in more than one tier. Human nature being what it is, the attention a cell receives will be inversely proportional to the trouble involved in looking after it; and it is well known to the makers that the first cells to go wrong in a battery are almost certain to be those most awkwardly situated. For this reason there can be no doubt as to the folly of trying to save expense by stinting the accommodation provided for a battery; and any extra outlay in this respect is sure in the long run to be more than repaid by the reduction of the maintenance charges.

Large-sized cells in lead or lead-lined wood boxes, arranged in single tiers, merely need to be mounted on two or three stout timbers running the length of the row; or these may themselves rest on cross-timbers or low brick piers at frequent intervals, if it is desired to raise the cells somewhat further from the floor. When a double tier of heavy cells has to be erected, the upper longitudinal timbers are generally supported by uprights of cast iron, as they are less clumsy and occupy less space than wooden uprights of equal strength. Brackets are sometimes thrown out on either side of the uprights to carry planks which run from end to end of the row and form narrow platforms, along which the engineer can walk when examining the upper tier of cells. Plenty of head room must

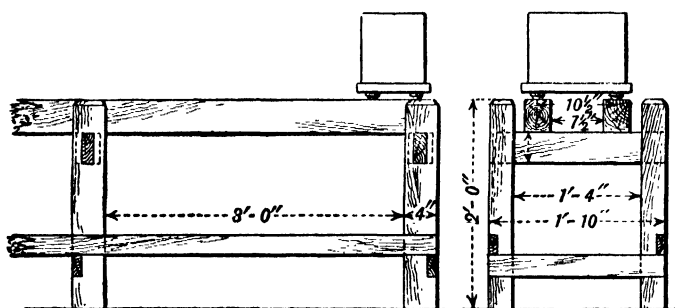


Fig. 159.—Stands for "Chloride" Cells.

be allowed above the lower tier, so that single plates can be lifted in and out of the cells without having to shift the boxes; but if the plates are burned up into sections which have to be handled all in one piece, it is generally found more convenient to remove the entire box from the stand, and so much clearance is not then necessary. Stands built entirely of wood are the usual practice for small and medium-sized cells. Their exact dimensions must, of course, be decided by the size of the cells to be erected and the nature of their connections; but the accompanying illustrations of the regulation stands used for two or three well-known makes will show the mode of construction generally adopted and the proportions of the various parts. Fig. 159 is a single-tier stand for a single row

ERECTION AND REGULATION OF LEAD CELLS. 300

of RG type "Chloride" cells. Fig. 160 is a two-tier stand for a double row of "Pritchetts and Gold" cells in glass

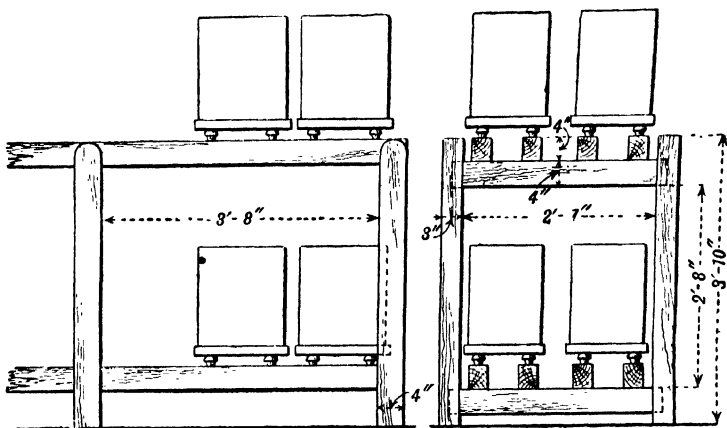


FIG. 160.—Stands for "P. and G." Cells.

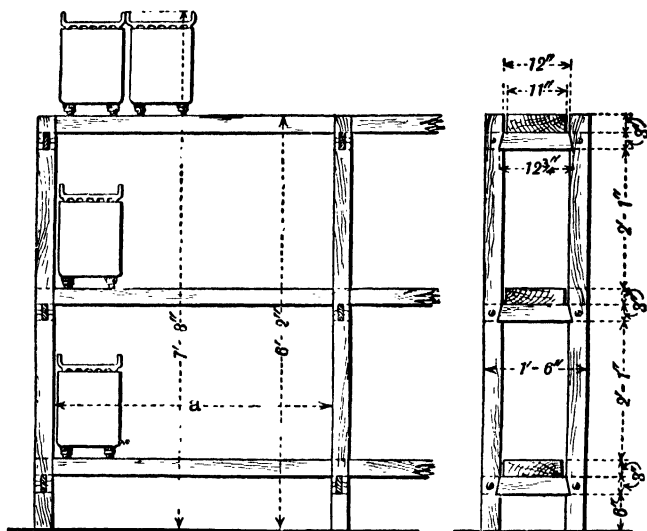


FIG. 161.—Stands for "D.P." Cells.

boxes. Fig. 161 is a three-tier stand for single rows of "D.P." cells in glass boxes. In the first two cases each row

of cells rests upon two timbers which run the length of the stand. These are supported by cross-pieces 3ft. to 4ft. apart, and they in their turn are morticed into the uprights. No difference has to be made in the design of the stands for cells containing different numbers of plates, but the total length of stand required will have to be proportionately varied. In the three-tier stand illustrated, an 11in. plank is substituted in place of two timbers to carry the cells. Moreover, the pairs of uprights are too near together to allow a cell to pass between them, and the dimension marked *a* must be altered according to the length of cell to be accommodated, so that a definite number will just go into the intervening space, whose average length is about 4ft.

Stands should be made of sound pitch-pine, pinned together with dowels of hard wood and well covered with some acid-resisting paint or varnish. In the case of three-tier stands it is generally advisable to let the uprights into the floor, or to prolong them upwards and fix them to the roof, or to take some similar precaution against their being overturned; but with one and two-tier stands—especially if the cells are in double rows—it is not usually necessary, although the contingency should always be considered.

Owing to the spray which is given off by a fully charged and gassing battery, and which soon covers everything in its immediate neighbourhood with a film of acid moisture, it is imperative that every cell should be separately and effectively insulated from the stand, for were this not done the battery would soon discharge itself when on open circuit by leakage of current between one cell and another; and serious consequences might result from leakage to earth in cases where the battery formed part of a large distributing system for lighting or traction purposes. Each cell is, therefore, stood upon glass insulators of the well-known "mushroom" or "petticoat" pattern shown in Fig. 162. The lower half constitutes a shallow circular tray in which is placed a few drops of a non-evaporative non-drying insulating fluid such as resin oil, and in this rests the inner rim of the upper half—a sort of inverted tray or cover with an overhanging lip. By this device not only is a layer of oil interposed in the path of leakage, but this layer and the adjacent surfaces of the glass

are all well protected from any direct access of acid moisture. Inexperienced folk are occasionally misled by what appears to be the most stable mechanical arrangement, and erect the insulators with the smaller half uppermost; but it is evident that in so doing they partially neutralise the benefits to be derived from their special shape. The correct position is as illustrated.

Three, four or six insulators may be used to each cell according to its size, but four is the usual number. If the battery requires to be specially well insulated, as may be the case when it is working on high voltage circuits, the whole stand should also be placed upon porcelain insulators, similar in design to those just described but of a larger size.

Lead or lead-lined wood boxes stand directly upon the insulators, which are so arranged as to receive the bearers or strengthening pieces crossing their bottom. Glass boxes are

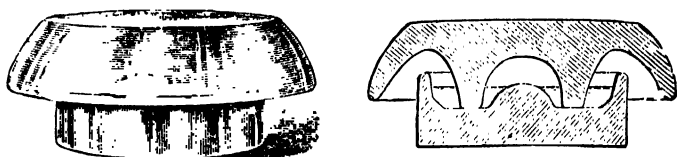


FIG. 162.—Oil Insulator.

generally too uneven to be treated in this way, for the whole weight of their contents being concentrated on a few points, some of them would almost certainly be fractured. The usual plan for minimising this danger is to stand a shallow well-varnished wooden tray, containing sawdust, upon the insulators, and the box upon the sawdust, which beds down and distributes the strain more or less evenly over the whole of the bottom. The tray is made somewhat larger than the box and projects about an inch all round it, as shown in Figs. 159 and 160. This method has the drawback that the sawdust soon becomes soaked with acid spray, and the damp mass rapidly deteriorates the trays. For this reason they are sometimes replaced, especially for small cells, by two thin strips of wood resting across the insulators. The cells in Fig. 161 are mounted so.

The Tudor Accumulator Co. employ neither trays nor strips, whatever size the glass boxes, but merely place a lead washer

about $\frac{1}{8}$ in. thick upon the top of each insulator. They find this is quite sufficient to prevent breakage, but a good deal no doubt depends upon the quality of the boxes themselves.

Instructions as to the best way of erecting any particular type of battery should always be obtained from the makers, for it generally happens that there is a certain method of procedure, only to be arrived at by experience, and depending on the number, size and kind of electrodes and the way they are mounted and connected, which enables the work to be got through much more expeditiously than any other. For cells not containing more than about 30 plates of small or medium sizes, all the electrodes of similar polarity are usually sent out already burned to their main connecting bar, and they then have all to be handled as one. The positive and negative sections are either lifted separately and placed in position in the cell box, the separators being inserted between the plates afterwards, or they may be put together outside and then lowered into the cell by means of lifting hooks, or by straps which pass under the plates and can be withdrawn when the section is in position. In some cases the manufacturers send out the sections all ready fitted and clamped together, but the tendency nowadays is in the opposite direction—namely, to supply all the plates separately, and to connect them to the main bars after they are set up in the cell.

Undoubtedly *the* method of joining plate to plate and cell to cell is by lead-burning them, so as to eliminate all other metals from the neighbourhood of the battery and ensure connections of uniform and permanent conductivity between every part. This plan is almost invariably adopted for central station or other large batteries; sometimes for the medium sizes of cells used in private plants and elsewhere; and occasionally even for the smaller portable cells employed for train lighting or traction purposes. Its drawback is that it necessitates the attendance of a lead-burner with all its paraphernalia, not only for the erection of a battery, but every time a single cell has to be taken to pieces for cleaning or repair, so that its application is limited more by the size of the installation than of the individual cells.

Where lead-burning is not practicable, and the plates are supplied already connected up into sections, one of the best

methods of uniting the lugs of adjacent cells is by soldering them. It is, however, seldom tried, because some absurd notion seems to have got abroad as to the uselessness and danger of solder for such purposes, and it is passed over in favour of devices which often prove many times more harmful and less efficient. Two well-tinned lead surfaces may be perfectly soldered together over a far larger area of contact than could be joined by lead burning, except with great difficulty; and when required they can be again separated in a very few minutes. With ordinary care and experience in the use of the iron or blow-lamp a neat joint can be made, which, after any superfluous metal squeezed out at the sides has been removed with a rasp, exposes practically no solder to view, and can be further protected with a little paraffin wax applied before the joint is cold. As a matter of fact, in cases of emergency the plates themselves can be repaired or connected up by soldering, and the joints will be extremely slowly attacked, whether under or above the electrolyte.

Lugs are usually clamped together by passing a brass bolt through two corresponding holes in their extremities, and screwing a nut and washer on either side. Considerable pressure has to be put on them to draw the two lead surfaces, previously well cleaned, into thorough contact so as to exclude the air and acid fumes. Fig. 163 shows Highfield's patent connector, in which the washers are provided with several concentric ridges, which dig into the lug and enable this object to be more fully assured. These, and sweating thimbles on the same principle, are supplied by the Chloride Electrical Storage Syndicate.

Although good brass is but little affected by long periods of immersion in dilute sulphuric acid, it is rapidly attacked by acid when exposed to the air and in contact with another metal, such as lead, electro-negative to itself, with which it forms a galvanic couple. All brass connections must, therefore, be protected as much as possible. This is usually done by painting or coating them with paraffin wax, or smearing vaseline over them, but none of these methods are thoroughly effective unless great vigilance is exercised; and, sooner or later, the bolts and nuts become more or less corroded. Basic sulphates of zinc and copper are formed

and may easily get into the electrolyte, where the copper will be deposited in a spongy state on the negative active material and give rise to local action which tends to depreciate the cell. A minor trouble is that the nuts sometimes get set on the bolt and can only be removed or tightened up with considerable difficulty. Of late endeavours have been made to provide a more perfect protection for the connectors by encasing all their exposed parts in lead or some hard lead-antimony alloy. Fig. 164 shows Rooper's patent connector, which is of this kind. The nuts have a winged covering of alloy cast round them, and when they are screwed up tight

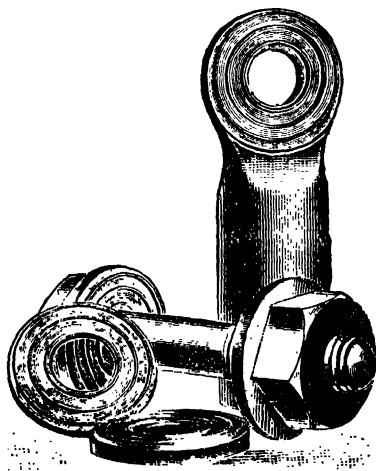


FIG. 163.—“Highfield” Connecting Bolts and Thimbles.

against the lugs to be joined, the bolt is enclosed in a complete sheath and so well protected that it may be of iron, although that metal is most susceptible to oxidisation by the least trace of acid.

Pure lead is too soft for the construction of nuts and bolts, but they are sometimes made from a lead-antimony alloy. These withstand the acid well, but have little mechanical strength, and on tightening them up the bolt frequently snaps or strips its thread. For this reason it is advisable to use in the first place a brass or iron bolt and nuts to

draw the lugs as tightly together as possible, then to remove these, taking care that the lugs do not shift their position, and insert the permanent one of alloy.

The Author has found that most of the corrosion of brass nuts and bolts may be obviated without a lead covering if they are insulated from contact with the lug by means of flanged collars of fibre, much as the brush-holders of dynamos are treated. Of course the bolt is then prevented from taking any part in conveying the current between the lugs, but this is not its proper function, and the contact between the two lead surfaces ought always to be sufficiently large and good to do this unaided. This remedy will be

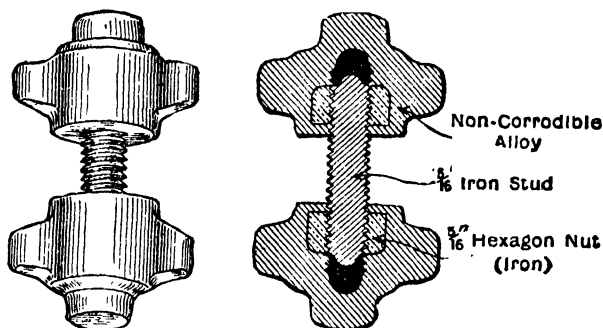


FIG. 14.—“Roofer” Cell Connector.

of little use however if the brass is poor stuff containing an excess of zinc or whose component metals are not properly combined; and this is often the reason why connectors are so easily attacked.

There are either commercial or technical objections to the use of most metals, other than brass, as cell connectors. Aluminium has often been tried, but is quite useless, as it is destroyed in a very short time.

When cells not very far apart have to be bridged together, as in passing round the corners of stands or from one tier to another, stout lead strip is best suited for connecting pieces.

First Charging.

The first charging of a battery is an operation of considerable importance, for, if not properly carried out, the cells may be irretrievably injured, and their output, efficiency and durability will all suffer in consequence. Electrodes containing applied active material are generally much more susceptible in this respect than those which are Planté-formed. The active materials, especially the negative, owing either to their being unformed or to their long exposure to the air after leaving the forming tanks, are in a condition very favourable to their rapid sulphation as soon as the electrolyte is added to them, and if this is allowed to proceed too far, it is difficult to counteract afterwards. For this reason the acid should on no account be put into the cells until the generating plant has been tried, all connections made to the battery, and everything is in readiness to proceed with the charging; and once the filling up has commenced it should be pushed through as fast as possible.

Dilute sulphuric acid is generally provided of the strength prescribed, and the pure acid is not often "broken down" on the spot except for quite small batteries or in places to which the cost of carriage is very heavy; but if it has to be done the mixing must be completed and the solution allowed to become quite cold before it goes into the cells. Warm acid aggravates the preliminary sulphation, and may give rise to a very violent action. When diluting, always add the acid to the water and keep stirring all the time. It should be poured in slowly and carefully, otherwise there is a risk of its splashing back into the face and eyes. The mixing vessel must be capable of withstanding boiling heat. Acid spots on the clothes are best neutralised with a drop or two of liquid ammonia, which will generally restore the original colour, and, if applied immediately, save even cotton fabrics from destruction. Woollen goods resist the acid longest, and it pays to wear overalls or an apron and sleeves of good flannel or baize when dealing with it. If the hands are likely to be immersed or come much in contact with the acid, rubber gloves should be worn. A strong solution of washing soda is most convenient for washing down stands, &c., on which acid may have been spilled, but chalk or whitening answers better if the acid is

upset on the floor from broken ⁴cells or other causes. Not only is the acid killed, but a pasty mass is formed which can easily be swept up.

The relative proportions by weight of acid and water which will yield a solution of any desired specific gravity have already been given on page 278. Fig. 165 is a curve showing the proportions by volume; but when mixing by means of the hydrometer only, or if checking the results in this way, it must be remembered that, while hot, the solution will read about 0.2 lower than it does after cooling. Should the makers' instructions as to the proper strength of acid not happen to be available when a battery is set up, a density of about 1.170 is the safest to employ, as this allows a margin for a rise of density by the time the first charging is finished.

Pouring or siphoning the acid direct from the carboys into the cells is a rather clumsy business, which generally results in a good deal of it being delivered over the connections or on the floor and other places where it is not wanted; and it is well worth while to employ a pump consisting of a rubber cap which fits over the mouth of the carboy and is connected by a pipe with a foot bellows. The delivery pipe passes through the cap and down to the bottom of the carboy. Pumps of this kind may be obtained from the manufacturers or from chemical apparatus makers.

The charging should commence immediately the filling up is concluded, and should continue without interruption. Before switching on the dynamo for the first time it must be ascertained with certainty if its connections are arranged so that its polarity is opposed to that of the battery—that is to say, positive to positive. The manufacturer's directions must be consulted with regard to the proper current strength, time of charging, final specific gravity and P.D., and other details connected with the first charge, for in these respects different types of cells require very different treatment. The charging may have to be maintained for any time from 12 to 48 hours at a current not exceeding the ordinary 10-hour rate. As a rule, the density of the electrolyte begins to fall the moment it is put into the cell, and continues to do so at a decreasing rate for some long while after the charging has commenced; but

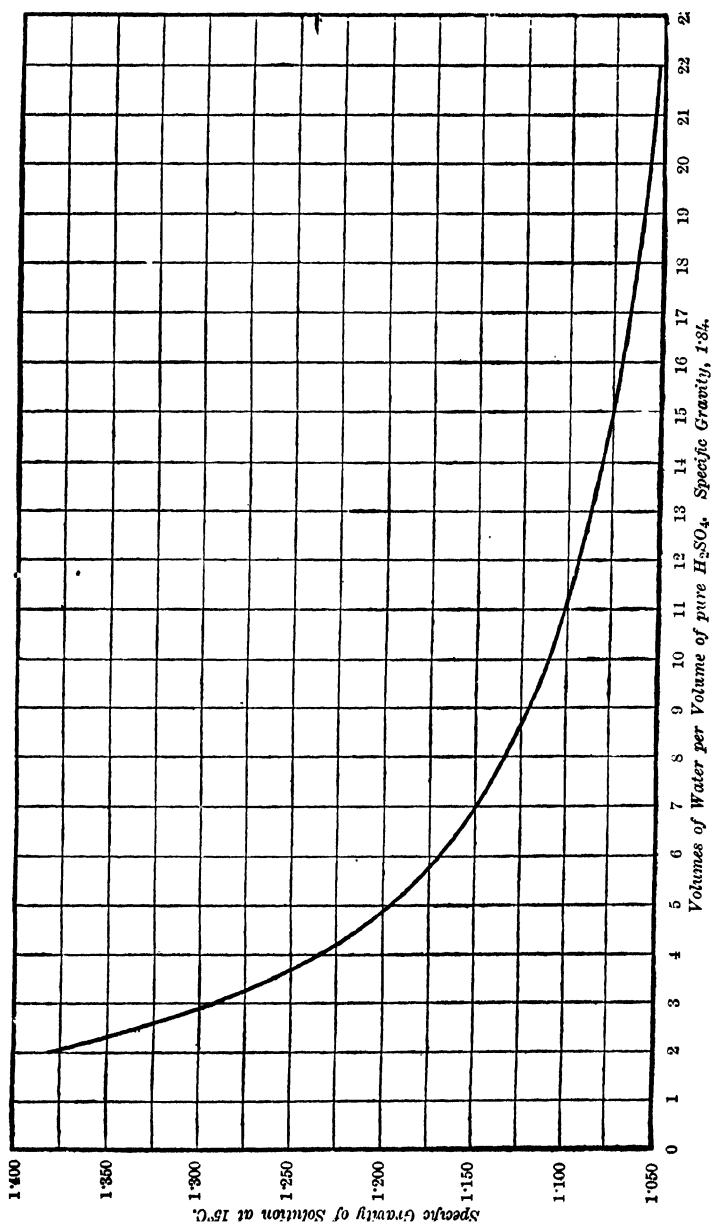


Fig. 165.—Curve of Dilution of Sulphuric Acid by Volume.

presently the desulphating effect of the current overpowers the sulphation by local action, a rise of gravity sets in, and eventually the electrolyte is restored to its original strength. This, however, is in itself no certain indication that the charge can be discontinued, for the active materials generally start with more or less sulphate in their composition, and by the time it is all eliminated considerably more acid may have been returned to the solution than was at first taken from it. A surer guide as to entire desulphation is afforded when the specific gravity—and also the P.D.—attains to a permanent value, but this should be separately ascertained for each cell, as in cases of defects or irregularities in the manufacture some may either reach to a much higher figure than others or take a much longer time in rising to the same figure. It sometimes happens that plates containing large percentages of active material very heavily sulphated can hardly be brought into thorough condition by one charge only, however prolonged, and the acid in the cells is found to increase slowly in strength for the first half-dozen charges or so. Indeed, it may be more convenient for other reasons not to attempt to prolong the first charge to its utmost limits, but to let the battery have a few light discharges, each followed by an extra thorough re-charge; and this treatment is often necessary before the full output can be obtained from the cells.

Finally, when the whole electrolyte has reached its maximum density it can be adjusted throughout the cells by adding water to any above the prescribed limit, or stronger acid—not over 1.4 specific gravity—to any below it. This operation should not be necessary at all with electrodes of uniform manufacture, but, on the other hand, if the acid in certain cells rises abnormally it is advisable to reduce its strength even before the first charge is completed.

Hydrometers.

- No battery installation can be considered complete without a supply of hydrometers. In some cases each cell has its own always floating in the electrolyte, so that the density can be read at any moment. More usually, however, there is only one hydrometer to every so many cells, or perhaps half-a-dozen for the whole battery. If only one or two are kept in

use at the same time; there should certainly be others in reserve, for being so fragile and easily broken, the battery may otherwise be left without any at all, and consequently suffer. Fig. 166 illustrates the type of hydrometer ordinarily employed. Its speciality is the flat bulb—not more than about $\frac{3}{16}$ in. through at any part—which enables it to float freely in the narrow spaces between the electrodes or close to the edges of the containing box. The scale is often marked so as to indi-

FIG. 166.—Cell-testing Hydrometer.

cate the points of maximum and minimum density, and the range travelled over between normal discharge and re-charge; but it must be remembered that these do not necessarily hold good for any cells except those in which the instrument was intended to be used.

Owing to the hydrometers having to be made so small and slight it is difficult to obtain an open scale for accurate reading. Fig. 167 shows a type of instrument made by J. F. Hicks, and designed to overcome this trouble. The scale is engraved on an enamelled stem which has a hole at its base, and is open at the top so that the electrolyte can rise inside it. The varying displacement when different lengths of the stem are immersed is therefore only determined by the space occupied by the glass itself and not, as is usually the case, by the



FIG. 167.—“Keating” Hydrometer.

volume it encloses; so the comparatively slight changes of specific gravity which occur during charge and discharge can be spread over the entire length of the stem.

Fig. 168 illustrates another kind of density indicator which can only be introduced into cells with glass boxes, and only gives approximate readings, but is very useful in unskilled hands or whenever it is desired to see the state of the electrolyte at a glance. It consists of a flat glass tube or case with

holes at intervals all up its sides and terminating at the top in a bent tube which forms a hook for hanging it on the side of the box. Within the case are four specific-gravity beads, each of different coloured glass and adjusted to float in different strengths of acid, which are marked upon them.

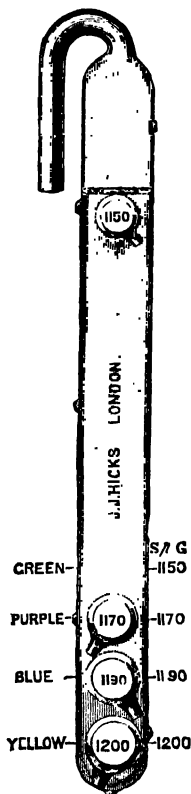


FIG. 168.
Hydrometer with
Specific-gravity Beads.

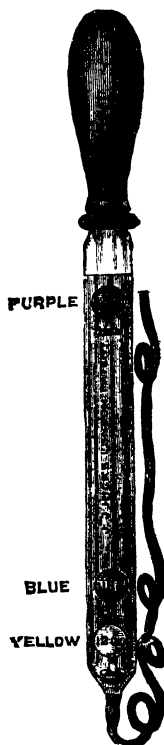


FIG. 169.
Hydrometer for
Sealed Cells.

These rise and fall with the charge and discharge, and the reading at any moment will be something between that of the lowest at the top and the highest at the bottom.

A modification of this arrangement, for use where there is no room to insert a hydrometer or when the cells have sealed-in

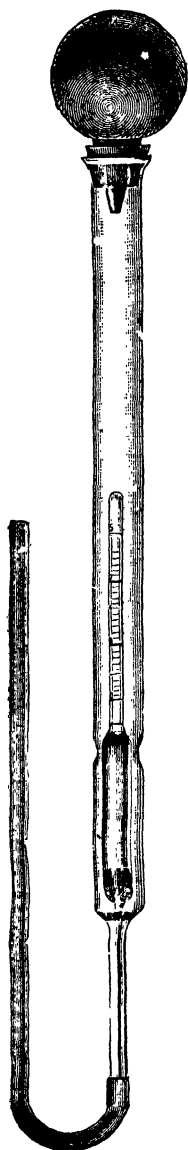


FIG. 170.
"Hurst"
Hydrometer

lids, as is often the case with portable or with traction batteries, is shown in Fig. 169. The case containing the beads has only two openings, one at the bottom joined to a length of rubber tubing for dipping into the electrolyte, and one at the top fitted with a rubber bulb. Upon squeezing the bulb and then allowing it to expand, the liquid is drawn up into the case and, after a reading has been taken, it can be forced out by again squeezing.

Hurst's enclosed hydrometer, supplied by the E.P.S. Company and illustrated in Fig. 170, is on similar lines but is intended for more accurate work.

Cell-testing Voltmeters.

A reliable voltmeter for taking the P.D.s of single cells is equally as essential to the equipment of a battery as are hydrometers. The instrument should read to 3 volts, and the scale, from 1.5 volts upwards, should be sufficiently open to be divided into tenths of a volt, and each division at least sufficiently wide to be again approximately subdivided by eye into quarters or tenths. It should also be fairly deadbeat and of high resistance so as to minimise the effects of bad contacts at the cell terminals. If of low resistance, it will be difficult to get steady and correct readings on this account.

Amongst the cell-testing voltmeters on the market a variety of devices are employed to ensure that the temporary connections from the instrument to the bars of the cells shall be as perfect as possible. The E.P.S. Company use a wooden rod carrying two tightly-fitting brass sleeves, one at either end and each connected to

one of the flexibles from the voltmeter terminals. The sleeves are screw-threaded on the outside so as to cover them with a series of ridges which cut through the oxidised and badly-conducting surface of the metal and reach the clean lead underneath.

Fig. 171 gives a cell tester of the permanent magnet moving-coil type made by Nalder Bros. and Thompson. A leather strap, through which the hand can be slipped to obtain a

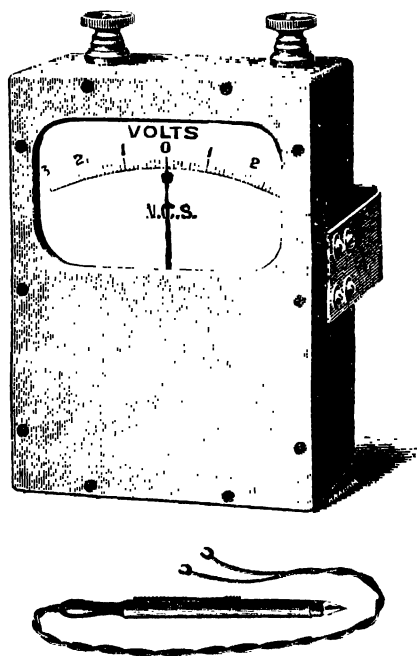


FIG. 171.—Nalder Bros. and Thompson Cell-tester.

convenient hold while testing, passes round the back, and the connecting bar has a metallic spike at one end and a piece of toothed metal along one side for making the respective contacts.

Fig. 172 shows a cell tester, also of the moving coil type, made by Evershed and Vignoles. In this instance there are two spike contacts with barbed points, one attached to the instrument direct, and the other, fitted in a handle, through a length of flexible wire. Both spikes can be detached to allow

the voltmeter to be packed in a small leather case. Instruments with spikes somewhat similarly arranged are also supplied by Kelvin and James White and by the D.P. Battery Co.

Although it necessitates cramping up the scale it is usually found most convenient for cell testers to read on either side of a central zero according to the direction of the current. In one type of the "D.P." instruments, which indicates in one



FIG. 172.—Evershed and Vignoles Cell-tester.

direction only and has a very open scale, a small reversing switch is provided in such a position that it can be worked by the hand holding the voltmeter.

Automatic Cut-in-and-out Switches.

It may occasionally be desirable to introduce into the charge or discharge circuit of a storage battery, switches or cutouts which shall be automatically operated if certain contingencies arise, or sometimes, in place of or in combination

with the switch, a relay circuit containing a bell is actuated in order to give notice that something requires attention; but, with the exception, perhaps, of a maximum cutout to stop the discharge if an excessive demand likely to injure the battery is made upon it, they are seldom wanted, and the apparatus they involve is of general application and does not need description here.

There is one case, however, which constantly occurs in isolated installations, where an automatic device quite special to its purpose is most useful, and, indeed, almost indispensable, if the plant is run by untechnical hands. When proceeding to charge a battery from a shunt-wound dynamo, the speed of the engine or the resistance in series with the field coils must be so adjusted that, at the moment of closing the circuit, the machine gives the same or a slightly higher E.M.F. than the cells, and this has to be ascertained by means of a voltmeter coupled up to a two-way switch. If the circuit is made while the charging E.M.F. is below that of the battery, the latter will proceed to discharge back through the dynamo and drive the engine. If, on the other hand, the E.M.F. is too high, there will be a large rush of current, which may blow the fuses or pull the engine up with a jerk, perhaps throwing off the belt or possibly breaking it. Even after the charging has been satisfactorily started, should the boiler pressure be allowed to drop or the engine to slow up from any other cause, there is always a likelihood of the current being reversed and continuing so for a long time without being noticed. All these possibilities are avoided by introducing into the circuit a switch which automatically closes it at the right moment and opens it again should the current at any time fall to zero. In its simplest form this may be contrived by some arrangement of a soft iron core working within a solenoid connected with the dynamo, and wound to come into action whenever its E.M.F. rises above or falls below a definite figure; but this does not nicely adapt itself to the varying voltages which have to be dealt with at different stages of the recharge, or according to the number of regulator cells in circuit; and the best plan is a switch operated by the difference of E.M.F. between the dynamo and the cells, independently, within reasonable limits, of their actual values.

The "Nevile" automatic accumulator switch, for which Drake and Gorham are the sole agents in this country, is a very widely used cut-in and cut-out of this type. It is illustrated in Fig. 173. A pivotted lever arm carries a bar-shaped permanent magnet at one end and a metallic bridge piece dipping into two mercury cups at the other. Each cup connects to one of the terminals by which the switch is joined in the circuit between the dynamo and the cells, care being taken to arrange it so that the charging current shall enter at the terminal marked +. One pole of the permanent magnet oscillates between the poles of an electromagnet wound with a fine wire coil connected across the cups and the terminals, so that it is excited by the difference between

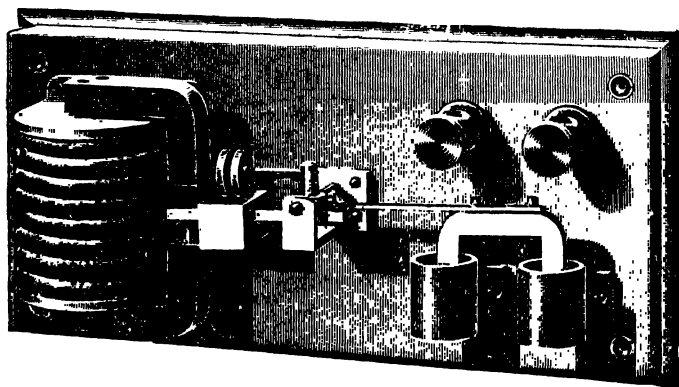


FIG. 173.—"Nevile" Automatic Cut-in-and-out.

the E.M.F.s of the dynamo and the battery. An ordinary switch, single or double pole, is also included in the main circuit, and, on closing this before charging, the coil receives a current due to the full E.M.F. of the battery—assuming that the engine has not yet been started—which keeps the bar magnet depressed and the bridge-piece raised out of the mercury in the cups; but as the dynamo is speeded up and its E.M.F. rises in opposition, the current through the coil gradually diminishes, ceases, and is finally reversed when the battery E.M.F. is overpowered. The bar is now repelled from the lower and attracted to the upper pole of the electromagnet, thus causing the bridge-piece to be lowered into the

mercury cups and complete the main circuit. Directly that happens, the fine wire coil of the electromagnet is short-circuited, but the charging current commences to flow, and passing through a series coil with which it is overwound, ensures that the bridge-piece is kept firmly immersed in the mercury. The automatic opening of the switch is simply a reversal of this procedure. If the dynamo fails to maintain the charging current, either temporarily and accidentally, or permanently because the engine is being shut down, the electromagnet ceases to be excited and the bar magnet drops by its own weight to the lower position, opening the main circuit and bringing the fine wire coil into action again as at first.

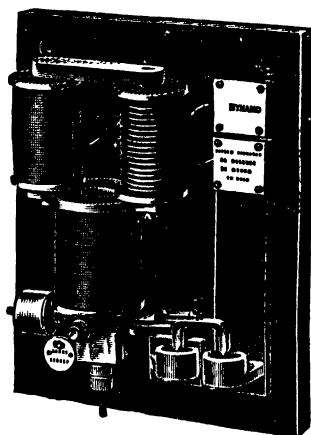


FIG. 174.—“Crawley” Automatic Cut-in-and-out.”

Fig. 174 shows the “Crawley” automatic switch, also of the differential type, manufactured by Nalder Bros. and Thompson. A soft iron core attached to the pivotted arm carrying the bridge-piece for the mercury cups works within the lower coil, which is excited by the battery E.M.F. as soon as the charging switch is closed. The upper left-hand coil receives the difference of E.M.F. between the battery and the dynamo, and directly the latter becomes the greater the core is repelled towards the right and closes the main circuit through the mercury cups, while the charging current circulating round

the thick wire of the upper right-hand coil holds it in that position.

In this instrument, besides the two terminals for looping it in the main circuit between the dynamo and the battery, a fine wire connection has also to be brought from the other pole of the battery to excite the lower coil. The ordinary charging switch must, however, be placed between this wire and the battery in order to prevent the coil from receiving any current except when it is closed.

Connecting-up.

The simplest application of the storage battery, and the one to which its use was chiefly confined for some years after its first introduction, is in isolated lighting installations for storing the current from the dynamo and supplying it at constant potential to the lamps as required. In many instances the whole of the current passes through the battery, which is drawn upon of a night until nearly discharged, and then recharged again during the day time. In other cases the battery, while serving the same purpose as before, is also arranged to come on the mains in parallel with the dynamo, so that they can share the load between them when unusually heavy, or that the cells can be charged without discontinuing the supply.

Fig. 175 gives, purely diagrammatically, the scheme of connections between a battery, dynamo and supply circuit—here supposed to be for lighting—so arranged that the dynamo *D* and the lamps *L* can either or both be switched on to the battery *B*; or the one direct on to the other, excluding the battery altogether. Three switches—shown as double pole—*bb'*, *dd'* and *ll'* are required for effecting the various combinations. If *dd'* and *ll'* are open but *bb'* closed, then the dynamo merely charges the cells. If *dd'* is open but *bb'* and *ll'* closed, the dynamo and battery are both connected in parallel across the mains, and the battery either charges, discharges or balances according to the regulation of its voltage. If *bb'* and *dd'* are open, but *ll'* closed, then the battery maintains the lights, the dynamo being cut out. Finally, if *bb'* and *ll'* are open but *dd'* closed, the dynamo takes the load direct, the battery being cut out. Should it not be desired to provide for

the last case, the switches dd' and their connecting wires can be omitted without altering anything else.

The voltmeter V is shown connected up to a double-pole two-way switch, so that it can indicate the E.M.F. of the battery or of the dynamo, according as the contact-pieces are to the right or left.

An ammeter, A , reads the current going into or given out by the battery. Sometimes two separate instruments, respectively connected in series with the switches b and l , are employed for measuring the charge and discharge currents; or one only

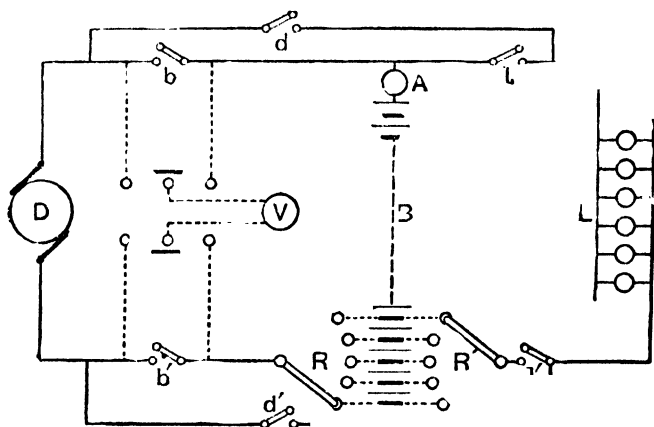


FIG. 175.—Battery Installation Connections.

may be made to serve the same purpose by means of a two-way switch. In small installations, where only single-pole switches are often used, a two-way switch frequently takes the place of b and d .

Regulating.

In many respects the endless amplifications and modifications that may be made in large installations and systems of electricity supply in the simple connections between generator, cells and supply mains just described are governed by considerations with which the battery has little to do, but there is one aspect of the matter closely related to the properties of

the cells themselves, and that is the arrangements and connections necessary to ensure an efficient regulation of the battery voltage. In nearly every application of stationary cells on any considerable scale, they work across mains which have to be—or preferably should be—constantly kept at a uniform, or nearly uniform, P.D., and as between the extremes of full charge and discharge the P.D. per cell may perhaps vary from 2·6 to 1·7 volts, it is evident that a means of regulation over a wide range must be provided.

Reserve Cells.

The method usually adopted is to instal as many cells as will be necessary for maintaining the line E.M.F. when they work at their lowest permissible P.D., and to arrange for cutting out, as required, such a number of these that the remainder will furnish the same E.M.F. when at their highest P.D. For this purpose all the cells are connected in series, and wires are brought off from the reserve or regulator cells to a multiple contact switch, by which the connection from one end of the battery to the discharge circuit can be shifted so as to exclude any desired number of them.

To charge the battery an E.M.F. sufficient to send a current through the whole of the cells must be available. It inevitably happens, however, that the reserve cells are discharged to a less extent than the rest of the battery, and in varying degree amongst themselves, some at the extreme end probably not having been drawn upon at all unless the previous discharge was very complete; and the connections to the discharge regulator switch have, therefore, to be duplicated to another similar one—the charge regulator switch—by means of which the cells can be cut out of the circuit as the charge proceeds, and each in turn gives evidence by its gassing, P.D., and specific gravity that it is quite full.

The simplest kind of accumulator switch consists of a number of contact blocks set out so as to form an arc of a circle whose centre is a pivot carrying a radius arm which can be put in connection with any one of them. This is the arrangement shown diagrammatically in Fig. 175. R is the charge and R' the discharge regulator switch. It will be

evident that as the radius arm is moved from block to block it must momentarily break the circuit if it leaves one before touching the next, or momentarily short-circuit the cell joined between them if it contacts with both at the same time. In all installations, therefore, where large currents have to be dealt with, a second arm is fixed alongside the first but insulated from it except for a connection through a small resistance in circuit between the two; and the contact blocks are so spaced that they cannot be directly bridged by either of the arms, but only from one to the other, through the resistance, which prevents an excessive rush of current but maintains the circuit.

The proportion of the cells that should be connected up as regulators varies with circumstances. If the battery is always disconnected from the mains when charging, the highest P.D. that need be provided for is little over 2 volts per cell, and with the ordinary fall of about 10 per cent. during discharge only one reserve cell will be required for every ten permanently in circuit. Such a case is exceptional, and more usually 25 to 33 per cent. of the cells have to be regulators to allow for the rise of P.D. while charging, although the total number of cells in the battery will not be greater than before. It is not obligatory that only one cell should be included between adjacent blocks of a regulator switch, and in plants where a very nice adjustment of voltage is not essential some that come into circuit when the P.D. is rising or falling rapidly are arranged in pairs or even groups of greater numbers.

When high voltages, heavy currents and a wide range of regulation have to be provided for, regulator switches develop into quite elaborate pieces of apparatus. In some, the contact blocks form a complete circle, perhaps with the sets for charge and discharge regulation arranged concentrically; in others, the fixed contacts are in a straight row and the radius arm is replaced by a sliding contact actuated by a worm wheel; and new designs are frequently being introduced.

When a battery is charged by increasing the E.M.F. of a generator, which at the same time has to deliver current at a lower P.D. to the mains, considerably fewer cells must be

connected to the supply circuit through the discharge regulator switch than are coupled to the generator through the charge regulator switch; and the consequence is that the *total* current passes into the cells intermediate between the two points. These excessive charging rates are undoubtedly one of the reasons why regulator cells so often go wrong before the remainder, and, to avoid this contingency, back or counter-E.M.F. cells are occasionally employed instead for regulating the voltage.

Counter-E.M.F. Cells.

A counter-E.M.F. cell is one whose electrodes contain no active material—that is to say, they are neither formed nor pasted. Plain lead sheets would serve the purpose, but it is preferable to use grids or grooved plates, so as to afford a larger surface for the evolution of gas. These dummy plates are mounted in dilute acid just like the others, and they oppose an E.M.F. of about 2·5 per cell to a current flowing through them, but without ever acquiring an appreciable capacity, for although the positives may form up in the course of time the negatives are unaffected.

As many of these cells are connected in series with the battery as will be necessary to cut down its maximum voltage to the normal level, and they are joined up to a discharge regulator switch so that they can be cut in or out of circuit just like reserve cells. No regulator switch is required for charging, because, as the whole of the cells discharge to an equal extent, they will all need the same amount of current to be put through them again, and the generator is merely connected to the end cells of the battery proper, and all current going to line branches off through the back E.M.F. cells.

Considering the absolute equality of work secured to each cell of a battery by the use of counter-E.M.F. cells, it is surprising that this method of regulating has not been more widely introduced into small plants; but for large installations it cannot compete with auxiliary generators or boosters, and these are now being more generally employed in preference to regulator cells. The most frequent application of a booster in conjunction with a storage battery is for obtaining the increased E.M.F. necessary for charging it without interfering with the running of the main generators at the normal P.D.

of the supply circuit. This plan also has the great advantage of not requiring a heavier current to be passed through any of the cells than is needed for charging them; but it is not a method of P.D. control at all, and either the reserve cells with their unequal conditions of discharge and elaborate regulator switches still have to be retained, or it may be combined with counter-E.M.F. cells as just described.

Booster Regulation.

In this system of P.D. control, the whole of the cells are always in circuit, charging or discharging; but the voltage of the battery is augmented or diminished by the addition or subtraction of an E.M.F. from a reversible booster in series with it of such amount that the sum or difference of the two is equal to the pressure across the mains. This supplementary E.M.F. also entirely determines the relations between the battery and the supply circuit. When the booster develops its maximum E.M.F. in the same direction as that of the cells they discharge their fastest; when the maximum E.M.F. opposes them they receive their heaviest charge; and between these two extremes any degree of charge or discharge can be effected, or the battery can be caused to balance the P.D. of the generators and remain quiescent.

The variations in the strength and direction of the current in the booster field circuit necessary to produce these changes are made by hand at the switchboard, and in this way the battery fulfils an additional and important purpose, for it becomes the equaliser of the load on the generators, and, through that, of the station pressure also. Further particulars regarding this and other arrangements of reversible boosters will be found in a Paper by Mr. J. S. Highfield.*

Automatic Regulation.

The idea of employing storage cells as an automatic load and pressure regulator is almost as old as their first commercial use, and the ability of a battery joined in parallel with the dynamo to reduce the flickerings of the lamps in lighting installations driven from gas engines were, and still

* "Storage Batteries in Electric Power Stations Controlled by Reversible Boosters," *Journal I.E.E.*, Vol. XXX., p. 1040, May 9, 1901; or *The Electrician*, Vol. XLVII, p. 290

are, frequently utilised. It was, however, soon recognised that only a limited extent of equalisation could be effected by this means, and that, unless the variations of engine speed were moderate, the battery large, and the distribution of load between itself and the dynamo suitably adjusted, the fluctuations of the lights still remained partially visible.

An electric tramway installation provides a case for automatic control of load and pressure of a different nature. Instead of the generators causing irregularities in the supply, it is the variations in the demand which re-act upon the generators. The current, going to line continually and rapidly, fluctuates between very wide limits, perhaps oscillating from almost no-load to several times the mean load in the course of a minute. This necessitates working under very inefficient conditions, with a plant much in excess of average requirements, and even then liable to be damaged by sudden strains before the governor of the engine can respond to them.

In 1894 accumulators were introduced on two traction systems—the Douglas and Laxey tramways, in the Isle of Man, and the Zurich tramways. In both cases reserve cells and switches were provided for adjusting the P.D. of the battery, according to its state of charge or discharge, to that of the line. Since that time storage batteries have been added to many tramway plants in this country, and to more abroad, for it is found that a suitable number of cells “float-ing”—as it is termed—on the line, either at the power house or in a sub-station, do very decidedly level up the load and pressure, and ease the generating machinery of some of the excessive calls which would otherwise be made upon it.

If a battery were without internal resistance, and its E.M.F. were constant under all conditions of charge and discharge, it would constitute a perfect automatic load and pressure equaliser when coupled across a supply circuit in parallel with shunt-wound dynamos. Presuming that these latter ran normally at the same E.M.F. as the battery, it would then “float” passively on the line; but, no matter how much or how suddenly the demand increased or diminished, it could furnish or absorb the difference, without any appreciable variation in the voltage of the mains or the load on

the generators. But as a battery must necessarily possess internal resistance, and an E.M.F. which varies owing to polarisation effects, its powers of regulation are limited. Directly it commences to discharge, its P.D. drops, and consequently it fails to take up the whole of the excess load; while on a diminishing load the opposite occurs.

If the battery is in a nearly but not quite fully charged state, the fall or rise of P.D. will be least, and will vary in approximately inverse proportion to the size of cell used or the current rate. If, however, the battery is in such a condition that an evolution of gas takes place on charge, or if it is too far discharged, the polarisation effects will be much more pronounced and the control not so good; nor will bigger cells or smaller currents then effect so great an improvement in the results. This is why even the comparatively large batteries often installed in lighting plants driven from gas engines do not always give an efficient regulation. Highfield finds that a battery balances best at 2.08 volts per cell, and then, that if it has an output of 450 amperes for one hour it falls or rises about 0.1 volt per cell with a current of 200 amperes in either direction.

Figs. 176 and 177 contain curves showing the effect of a regulator battery upon the generator load and pressure respectively in a traction plant. In each figure the upper and lower curves were obtained under precisely similar conditions, except that the one was before and the other after the installation of the battery. A comparison of the two brings out very clearly what may be seen in all similar diagrams—namely, that the battery ensures a very considerable improvement, but that a complete equalisation is by no means secured. In this instance the maximum variation of load is reduced from 270 to 50 amperes. These curves as well as the others given in the conclusion of this chapter are taken from a Paper by Mr. G. A. Grindle.*

As extensive storage is seldom required in traction stations it is generally too costly to put down batteries of large capacity in order to obtain a better regulation; and whatever the size of the cells, the result must, for the reasons just given,

* "The Use of Storage Batteries in Connection with Electric Tramways," *Journal I.E.E.*, Vol. XXX., p. 1098, Feb. 26, 1901, also *The Electrician*, Vol. XLVI., p. 779.

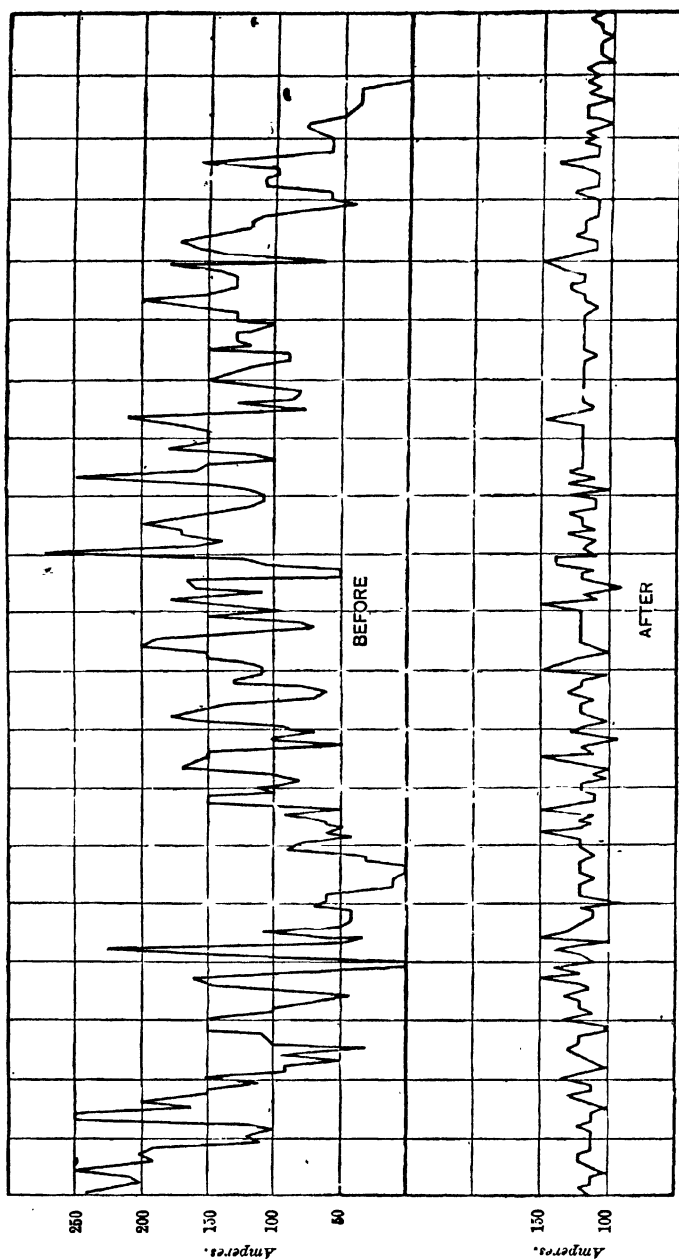


FIG. 176.—Load Variations before and after Storage Battery Use.

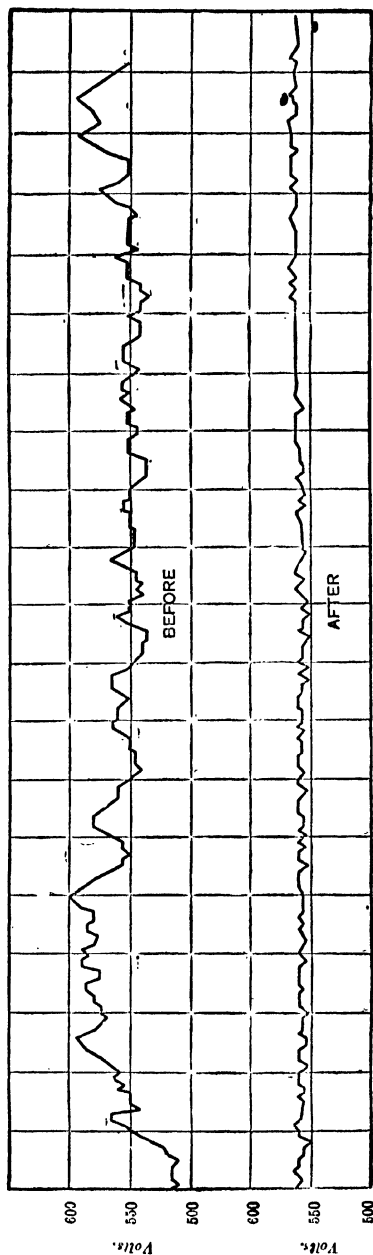


Fig. 177.—Pressure Variations before and after Storage Battery Use.

be far from perfect. The trend of modern practice is, on the contrary, to use a battery of comparatively small output and to work it at as high a rate as is compatible with durability, compensating automatically for its variation of P.D. by a booster connected in series.

A considerable variety of arrangements have been devised for accomplishing this purpose, all based on the principle of making the changes of voltage or current automatically vary the strength and direction of the booster's field magnetism and hence of the boost also. A certain amount of regulation

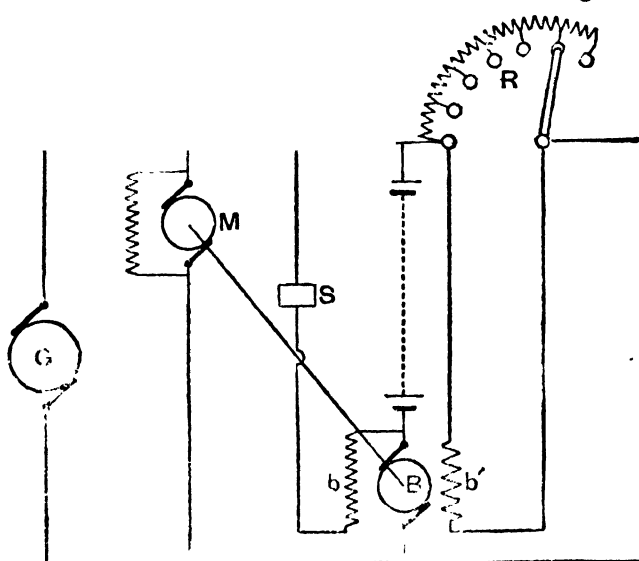


FIG. 178.—Differential Booster Connections.

can be obtained with series and compound-wound machines, but a special modification of the latter, described as long ago as 1890, and now termed a differential booster, yields better results. The shunt winding *b* is connected across either the battery or the 'bus bars, while the series winding *b'* is joined in the supply circuit as shown in Fig. 178. When the generators are delivering their full load to the mains the effects of the shunt and series coils neutralise each other so that the machine generates no E.M.F., and the battery neither charges or discharges. When the load increases, the series

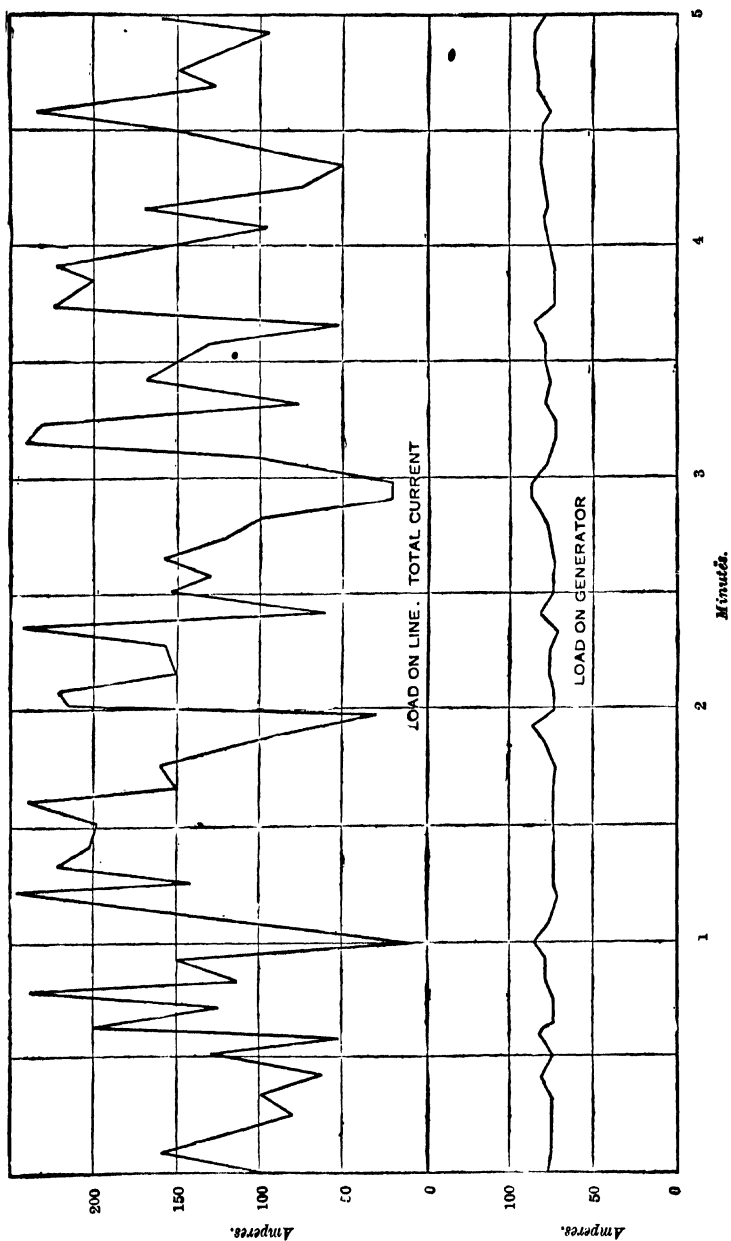


FIG. 179.—Curves of Load on Generators and Total Load in a Tramway System where Batteries are used.

predominates, the battery is boosted and discharges. When the load decreases, the shunt effects a reverse magnetism, the machine acts as a "crusher,"—to use an expressive Americanism—and the battery charges.

With a differential booster and driving motor of proper design, the load and pressure of the generators can be maintained practically constant under all variations in the external demand at any moment, but it does not compensate, or only partially, for alterations in the balancing E.M.F. of the battery as it becomes more or less charged or discharged. To do this a hand control is provided, so that the relations between the shunt and series windings may from time to time be readjusted. In Fig. 178 an adjustable resistance, *S*, is indicated in series with the shunt winding, and another, *R*, in the main circuit, off which the series winding is taken as a shunt. The latter is the one generally used.

Fig. 179 gives a good idea of the sudden and excessive fluctuations of supply which have to be dealt with in a tramway station, and also of how, by the proper use of a battery, the generators may be relieved of nearly all the strain and be kept working at a comparatively constant load. The readings were taken every five seconds for a period of five minutes at a time of heavy load.

The "Highfield" reversible booster is an ingenious arrangement, which not only corrects for all variations of battery P.D. caused by changes in the load, but takes into account those other alterations due to the condition of the cells; it therefore gives an entirely automatic control at every stage of working. The arrangement of connections is shown diagrammatically in Fig. 180. The booster armature *B* is, as usual, in series with the battery. Its field circuit *C* is coupled in series with the armature of a small exciting generator, *E*, and the two together are connected across the ends of the battery. Both the booster and its exciter are driven at constant speed by a shunt-wound motor, *M*, all three being on the same shaft, and the exciter is compounded so as always to furnish the same E.M.F. as the normal pressure on the mains; the number of cells in the battery is also so proportioned that they shall furnish the line pressure when at their most favourable E.M.F. for regulating purposes—*i.e.*, 2.08 volts

per cell. So long as the exciter and battery pressures are equal and balance each other no current will flow in the field circuit of the booster, it will develop no E.M.F., and the battery will simply float on the line. Whenever the battery E.M.F. falls, no matter whether through its becoming more discharged or because more current is demanded from it, the exciter will furnish a current proportional to the difference of the E.M.F.s, and the booster field windings are so designed that it will generate an E.M.F. proportional to its exciting current and equal in amount to the difference of E.M.F.s between the exciter and the battery. This E.M.F. is in the same direction as that of the cells, but if the battery E.M.F.

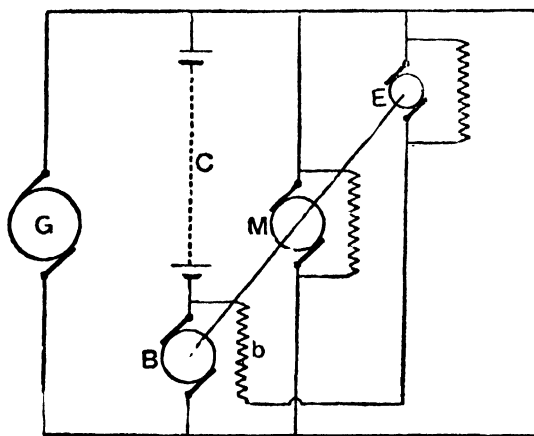


FIG. 180.—“Highfield” Booster Connections.

rises instead of falls, it overpowers the E.M.F. of the exciter, which is motored and receives a current in the reverse direction, and the booster E.M.F. then opposes that of the battery.

The net result is that the battery behaves, not only as if it had no internal resistance, but also as if polarisation on charge and discharge were entirely eliminated; and, in conjunction with the booster, it supplies current to or receives it from the mains at an almost constant potential. Fig. 181 affords an example of the relations existing between the load on the line, generator and battery, and the P.D. of the line, battery and booster respectively in a tramway installation

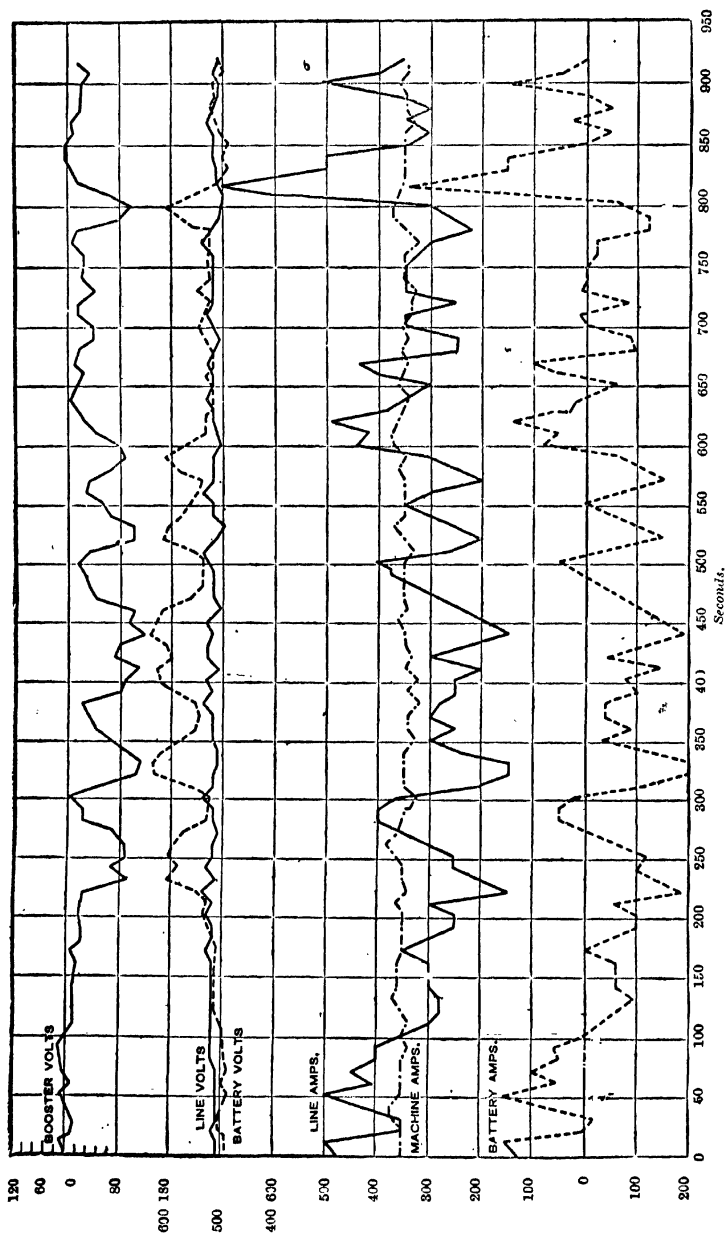


Fig. 181.—Curves from Generator, Battery and Special Booster on a Tramway Load.

worked on this system. It will be seen how closely the battery follows all variations from the mean load dealt with by the generator, and how nearly the booster P.D. compensates for the variations of battery P.D. so as to maintain an almost constant line pressure. To make this quite clear the battery curve is plotted—contrary to the usual practice—with its discharge *above* the zero line and its charge below it.

When a battery is installed in a tramway station in combination with a booster, it is usual to provide it of such a size that the maximum currents it has to deal with do not much exceed its one-hour rate, and it does most of its work, both charging and discharging, at something between that and the three-hour rate. It might naturally be thought that the electrodes would soon be worn out under what is ordinarily considered such severe conditions of usage, and the battery depreciate at a rate which must render its cost of upkeep excessive. Instead, it has been found that the cells last better than many which receive continuous discharges at much lower rates.

Although the automatic regulation of battery P.D. by means of boosters has been more especially developed to meet the requirements of traction stations where an entirely hand control would be quite incapable of following the rapid fluctuations of load, it can, of course, be equally well applied to other systems of supply to do away with the necessity for the frequent adjustment at the switchboard of the booster E.M.F. or of the number of reserve cells in circuit.

Occasionally an automatic device is combined with the reserve cell switches, and a variety of arrangements have been designed for this purpose. One of the best known of these is the Trumphy automatic regulator. The switches are controlled by an electromagnet coil acting as a voltmeter connected across the supply mains. As their P.D. rises or falls the core moves up or down, making contact and completing the one or another of two relay circuits. Each of these also contains an electromagnet which, on being excited, in its turn closes the circuit of a larger one, and when the core of this is sucked in it moves the switch arm from one contact to the next by means of a ratchet and ratchet wheel. In doing this the relay circuit is broken, but if the voltmeter

circuit is still closed, it is at once made again, and the switch arm is moved another step. By this means cells are cut in and out, according to which magnet is operated, until the normal pressure is restored and the voltmeter breaks circuit. In other types of automatic switches a small motor provides the power for actuating the pawls.

All such devices as these are necessarily too sluggish to deal effectively with the conditions existing on a traction circuit. On other large systems of supply they involve all the disadvantages of regulator cells, with further added complications of their own, while in isolated installations, where load variations do not, as a rule, much affect the P.D. and all that has to be compensated for is the fall of voltage as the cells discharge, the amount of regulation required is generally too little to need an automatic control at all ; but it is here, if anywhere, that their chief usefulness lies.

CHAPTER X.

PRESENT-DAY CELLS. '

"E.P.S." Accumulator.

The Electrical Power Storage Co. of Millwall was founded in 1882 to manufacture accumulators under the patents of Swan, Sellon and Volekmar. It soon afterwards acquired the rights in the Faure patents, and so held a practical monopoly for some years, until several makers commenced to turn out formed electrodes on a commercial scale. Its cells—generally known for short as "E.P.S."—have always contained pasted electrodes, both positive and negative, and, up to recent years, supports of the familiar through-grid type; but as regards their dimensions, the size, shape and relative proportions of their framing and apertures, and the means provided for connecting up and mounting, a great variety of designs have been brought out from time to time. A few particulars of each of the chief types now listed are given below.

The "P" type cells are lead-lined wood boxes containing the largest-sized electrodes—about 14in. square. They are specially designed to give rapid discharges, and can be safely emptied in one hour or less, so are very suitable for use in power-houses or similar purposes.

The "W S" type are intended for continuous discharges at anything up to a two-hour rate. Glass boxes are used for the cells of smaller capacity, and lead-lined wood boxes for the larger ones. The electrodes are about 9in. square. The "W T" is a type similar to the "W S," but arranged for use in low boxes for ship lighting and other purposes.

The "K" type may be discharged in $3\frac{1}{2}$ hours as a normal maximum rate, but this can be very considerably exceeded for short periods. The electrodes are approximately 9in. square, and are supplied either in glass or lead-lined wood boxes.

In all these three types of cell the electrodes have the same general design, but differ in the proportions of their parts according to the work they are expected to do. Fig. 182 shows a portion of a positive and Fig. 183 a portion of a negative of the "P" type. The positives have a central core of solid lead covered on either side with horizontal ribs, which slope

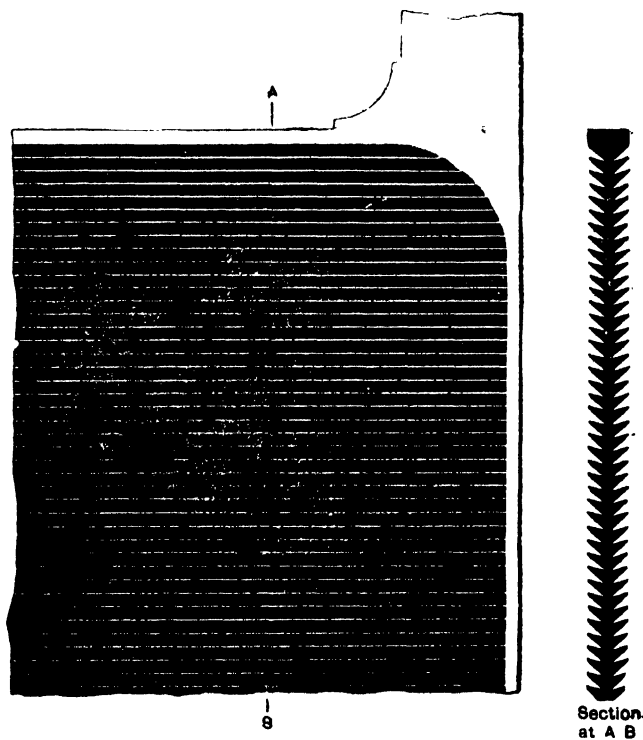


FIG. 182.—"E.P.S." Positive—"P" Type.

obliquely upwards so as to afford a better support to the active material. Although the metal in the electrodes is not so fully subdivided as in some makes which receive a Planté formation, yet it affords a very considerable surface, which undergoes sufficient formation during the ordinary working to maintain the output even if the paste should gradually

fall out owing to severe conditions of usage. The negative electrodes are through-grids having oblong cells with inwardly tapering walls, and are pasted in the usual way.

The electrodes of the "P" type cells are hung on vertical glass slabs, are separated by glass rods, and the plates of adjacent cells are burned direct to an intermediate connecting bar after the manner now generally adopted for large batteries.

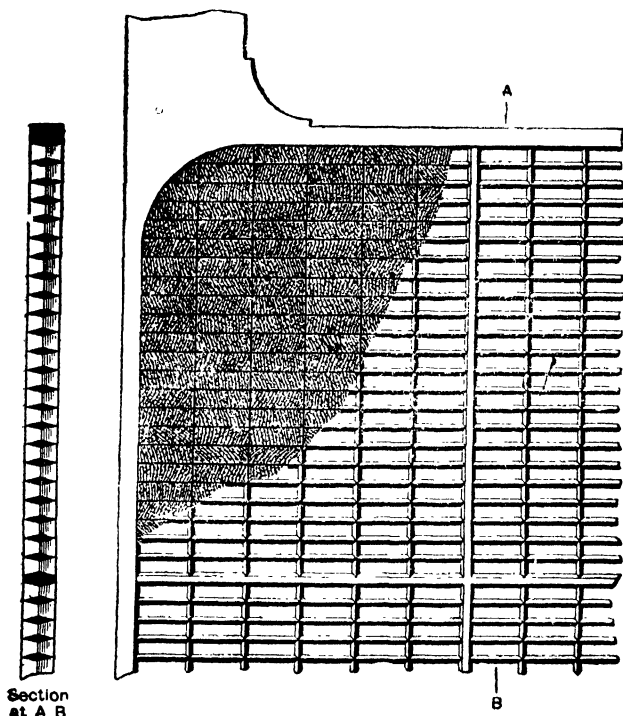


FIG. 183.—"E.P.S." Negative—"P" Type.

The methods of mounting the "WS" and "K" type electrodes are very much alike, and may be seen from Fig. 184, which shows one of the "K" type cells. A prolongation at each of the bottom corners of the negative plates is burned to one of two connecting bars running the length of the box, and from one end of these the main lug passes up through the electrolyte. Projections from the upper edges of the positives

are also burned to two bars which rest on ebonite insulating saddles placed upon the top of the negatives, and thus the whole section is suspended. Ebonite forks serve as separators for the "K" type plates, but for the "W S" type glass tubes $\frac{1}{4}$ in. in diameter are used, giving a somewhat wider spacing.

The "L" type cell is the modern survivor and representative of the "1888" type and still earlier designs for lighting and general use. Both the positive and negative electrodes are of the through-grid type, with apertures about $\frac{1}{4}$ in. square. They are about the same size, and have about

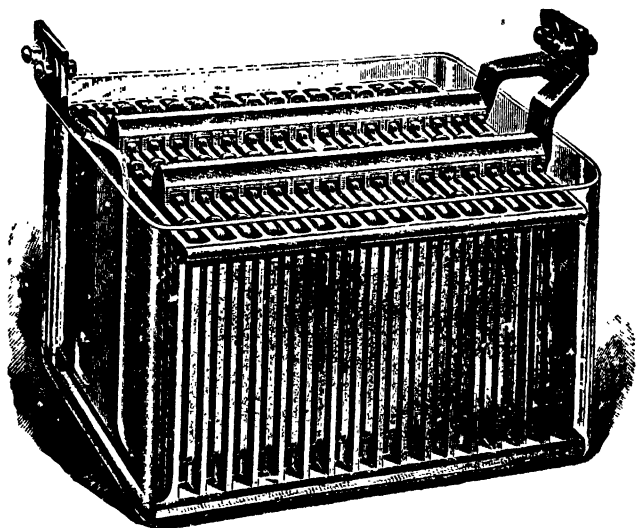


FIG. 184.—"E.P.S." cell—"K" Type.

the same output as the "K" type plates at slow rates, but their construction is slighter and they are not supposed to be subjected to rapid discharges. They are employed in isolated installations and other places where the discharge does not exceed a ten-hour rate. The negative section has an extra connecting bar at either side upon which the positives are supported by side lugs resting on insulating saddles.

The "E," "T" and "B" type cells all contain smaller electrodes than the "L" type, and are designed for traction or other uses where it is necessary to discharge them in about

three hours. They can be had either with ebonite or lead-lined wooden containing boxes. The "B" type is specially intended for launch work, and the boxes and electrodes are narrower at the bottom than the top. This sloping side often enables them to fit better into the limited locker space provided under the seats.

The "C" type cells are provided with long and very low electrodes, so as to go under the seats of railway carriages for train lighting.

The "V" and "Q" type cells contain small-sized electrodes, and are meant for use as portable batteries. Both types are also made up into sets of several cells in one containing box.

In 1896 the E.P.S. Co. brought out their "Faure-King" type of cell in order to meet the demand for a cell of large output and light weight suitable for use in electric automobiles. The original designs of the electrodes have already been described on pages 56-59. The forms of grid shown in Figs. 51 and 52 are not now used, but one approximating more nearly to Fig. 13, only with the prongs springing from the corners of each aperture instead of from the centre of its sides. Also, ebonite, by reason of its greater durability, has been substituted with improved results where celluloid used formerly to be employed.

The cells are made up with two different sizes of electrodes—"A" and "B" types respectively—and they give an output varying from 3.5 to 4.5 ampere-hours per pound of complete cell, according to the number of plates it contains. The best output previously obtainable from the "E" type traction cell, or, indeed, from any established type of cell then on the market, was about 2.5 ampere-hours per pound of complete cell; so this result was a very considerable improvement. The "B" type cells were used in some of the first electric cabs in London and Paris.

The "Moting" cell is a type having an output for weight intermediate between that of the "E" and the "Faure-King," and is also intended for traction purposes. It is only made in one or two sizes.

The table given below shows the ampere-hour output per positive plate for most of the various types of cell just described, and also the normal and maximum charging rates.

The maximum rate of continuous discharge for each type can easily be gathered from the column under which its output is entered :—

Type of Cell.	Output at Rate of Discharge in Hours.						Charging Rate.	
	1	2	3½	5	7	10	Maximum.	Normal.
P	50	...	88	...	105	...	25	12·5
WS	...	30	42	...	56	...	11	5·5
K	29	...	35	...	8	4
L	45	4·3	2
E	14	4	2
T	13	4	2
B	18	6	3
FK—A	38	7·6	...
FK—B	25	5	...

“Crompton-Howell” Accumulator.

The Crompton-Howell cell is not, strictly speaking, entitled to a place in a chapter on “Present-Day Cells,” its manufacture having been discontinued for some years; but as it was in many respects the pioneer of modern battery practice, and some of the plates may still survive in a few places, it deserves a passing reference. Both the positive and negative supports were cut from blocks of porous crystalline lead—prepared by a process already described on page 102—and then subjected to a Planté formation; after which those intended for negatives were reversed. The extremely large internal surface of the electrodes enabled them to endure rates of discharge which had previously been considered prohibitive, and from about 1887 onwards the cells were very much in evidence, being installed at Bradford and many other of the earliest central stations with the most excellent results. In these batteries was first generally introduced the method of connecting adjacent cells by burning their plates direct on to a common bar.

It would be difficult to say precisely why this type of cell did not always prove equally satisfactory, but it is evident that the peculiar structure of the electrodes must have rendered them specially susceptible to evil results arising from impurities in the metal or left over from the forming process.

"D.P." Accumulator.

The D.P. (Dujardin-Planté) cell was first manufactured in this country by Messrs. Johnson and Phillips under the supervision of Messrs. Drake and Gorham, and afterwards by the D.P. Battery Co., of Bakewell. Its introduction followed close upon the Crompton-Howell cell, and, like the latter, it also had both positives and negatives of the formed type. The construction of the plates was extremely simple. A number of strips of lead cut to a suitable length were grouped sideways together, but with a small space between

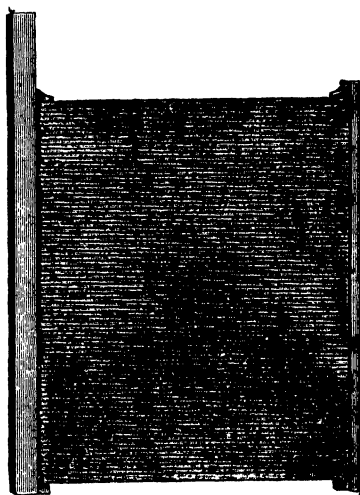


FIG. 185.—"D.P." Strip Positive.

each; and then connected up by casting bars of lead on to their ends. One of the bars, stouter than the other, formed the main conductor. The positives and negatives were alike in design, but differed in thickness—determined by the width of the strips. Fig. 185 shows a plate of this type. The surfaces of the strips were covered with a number of minute depressions or cells by passing the sheet lead between a pair of embossing rollers before cutting it up; the object being to afford a better hold for the active material. The Dujardin formation was effected in a bath of dilute sulphuric acid containing some alkaline nitrate.

After the formed electrodes had been burned on to connecting bars and built up with forked separators between them in

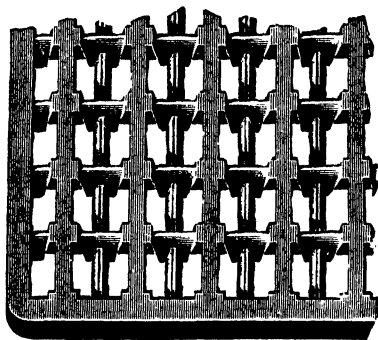


FIG. 186.—“D.P.” Grid Negative.

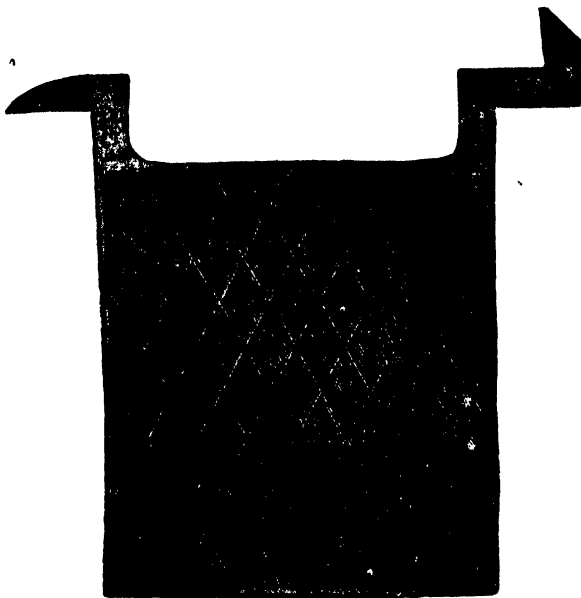


FIG. 187.—“D.P.” Diagonal Ribbed Positive.

the usual way, the whole section used to be bound rigidly together by two skeleton frames of hard lead alloy placed

outside the end negatives and connected by side strips of wood, which passed through slots in the frames and were held in place by metal pins or wedges. This arrangement enabled the section to be lifted in or out of its containing box without coming to pieces.

In recent years the formed strip negative has been replaced by a pasted type of plate with a cast grid support, a portion of which is shown in Fig. 186; and in some cases a cast positive with diagonal ribs—illustrated in Fig. 187—is used instead of the strip positive. With these more rigid electrodes the older method of mounting them has been abandoned in favour of the modern practice of hanging from the edges of the containing box, as shown in Fig. 188.

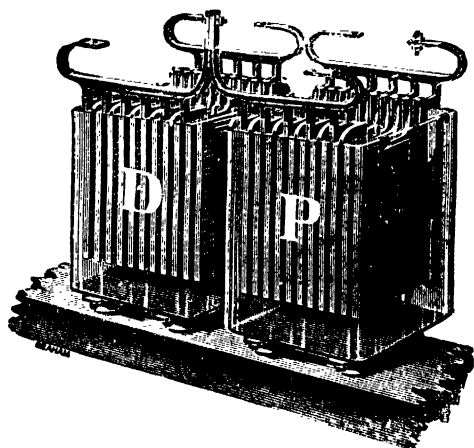


FIG. 188.—“D.P.” Cells.

“Epstein” Accumulator.

The Epstein cell was the first in this country of those having grooved electrodes with a central web of metal, although this type had been previously used abroad and has since become one of the most usual designs here. Its real speciality was the method of formation, invented and patented by the late Mr. L. Epstein, and this is still adhered to, as also is the use of formed plates for the negatives. The cell was originally manufactured by Messrs. Woodhouse and Rawson,

then by the Epstein Electric Accumulator Co., and now by Messrs. Rooper & Co.

The supports are cast in pure soft lead, and their mechanical strength and electrical conductivity are insured by a central web of metal as well as by horizontal, vertical and diagonal ribs. Fig. 189 shows a positive, and Fig. 190 a negative of the "C" type in plan and cross-section. The actual

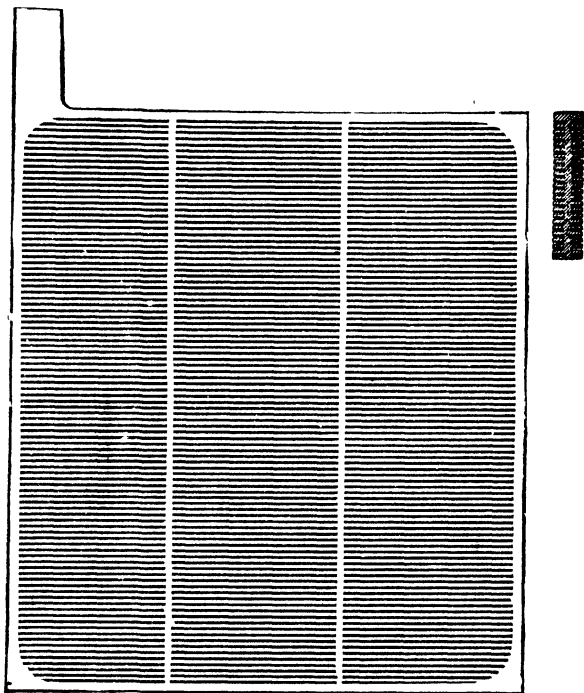


FIG. 189.—Epstein Positive—"C" Type.

exposed surface of an electrode is about five times its nominal surface or ten times the superficial area of one side. The formation is effected by boiling the plates in a dilute solution of nitric acid, drying in hot air chambers, and then subjecting them to a series of reversals in an electrolyte of pure dilute sulphuric acid. The makers state that with care, and a rigid adherence to the correct procedure, the nitrogen acids and oxides that may

at first be present are all reduced to ammonia by electrolysis, and it is found in practice that there is no risk of the disintegration of the supports due to traces remaining. They also say that the causes which a few years ago proved somewhat damaging to the merits of the cell have been eliminated, and it is now re-established at its former high standard of excellence.

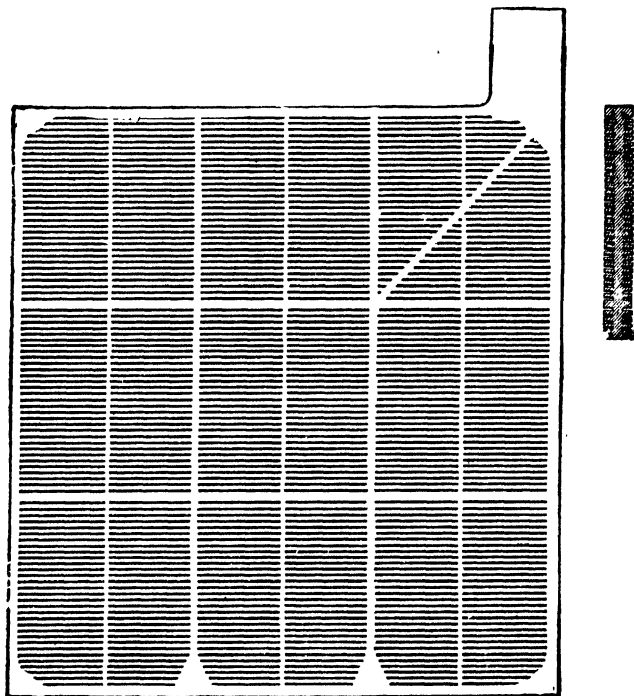


FIG. 190.—Epstein Negative—"C" Type.

Three stock sizes of electrodes are made: The "A" type, 12in. wide by 13in. high; the "B" type 9½in. wide by 10in. high; and the "C" type 7½in. wide by 8in. high. These can be sub-divided if necessary. The positives weigh 20lb., 11lb., and 6.5lb., and their outputs are 120, 72, and 50 ampere-hours respectively. Messrs Rooper & Co. have introduced a new method of connecting up the cells, and the

plates in a cell. This is illustrated in Fig. 191. Each plate is provided with a connecting lug, slotted at the end. The slots in the lugs from adjacent cells all fit over a long lead-coated bolt, which runs the width of the cells and carries lead washers which constitute spacing pieces between adjacent lugs. The washers and lugs are clamped tightly together by means of winged nuts screwing on to either end of the bolt

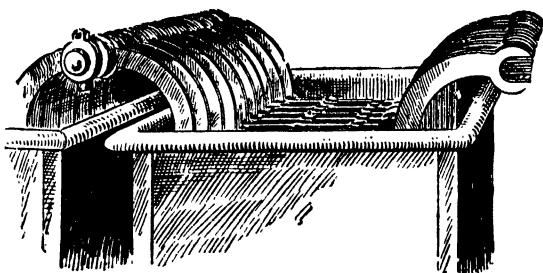


FIG. 191.—' Rooper ' Battery Connection.

and covered with some non-corrodible alloy. By this arrangement, mounting the cells is much facilitated, and any individual plate can be easily removed for examination or replacement, even while a current is flowing, without disturbing the remainder.

English "Chloride" Accumulator.

With the Chloride accumulator a new type of electrodes came into use, differing both from the Faure, or pasted plates, and the Planté, or formed plates. Some particulars of the early history of cast lead chloride as a raw active material have been given on page 17. Its employment was first developed commercially in France under the patents of Laurent-Cély, and in the U.S.A. under the patents of Payen, Currie and others; but when the Chloride Electrical Storage Company was founded in this country they were all combined into one system. The method of manufacture was not allowed to pass unchallenged by the Faure, Brush, or Swan interests, and the question of infringement of patent rights was raised in all

three countries. Here, the reference of the matter to the arbitrament of the law was only narrowly averted owing to the imminent expiration of the patent covering the grid type of supports.

The following is a brief summary of the processes involved in the construction of chloride plates as now practised at the works at Clifton Junction. The first stage is the preparation of the lead chloride itself. Powdered litharge is added to acetic acid in large vessels and is kept in a state of continual agitation until it dissolves and is converted into lead acetate. The solution then passes into settling tanks and from these into precipitating vats, where the quantity of hydrochloric acid necessary for the complete decomposition of the lead acetate is mixed with it. The lead chloride and the re-liberated acetic acid are next separated by means of a filter press, the former going to the drying ovens, while the latter is ready to be used over again.

The dry lead chloride is now weighed out with a certain percentage of finely divided metallic zinc and melted down in large pots capable of holding about 4 tons of the molten material. The zinc reduces a portion of the lead chloride with the production of zinc chloride and metallic lead, and thus a mixture of lead and zinc chlorides is obtained. The melting pots are of iron lined with refractory brickwork to protect it from the corrosive action of the molten chlorides, and the bottom is kept covered with about 6in. of lead for the same purpose. By means of a plumbago crucible, the chloride is ladled out of the pot and cast into hexagonal-shaped pastilles or tablets in an iron mould which holds about 70. The pastilles are as thick as the electrode of which they will presently form part, and about $\frac{3}{4}$ in. across, and each contains two small holes produced by pins in the mould. After removal from the mould, the pastilles are placed on similar pins in another mould which is simply recessed out to the shape of the complete electrode. It is then shut by a hydraulic press and molten lead forced in under a pressure of 150lb. per square inch by means of compressed air acting on the metal in a closed pan. The pastilles cannot shift on account of the pins, but remain firmly embedded at regular intervals in a framework of very

solid lead. Fig. 192 shows a portion of the finished plate obtained in this way.

The formation of the electrodes—that is, the reduction of the lead chloride, yet remains to be effected. It cannot be done by an ordinary electrolytic process on account of the large quantity of chlorine that would be evolved; so the unformed plates are immersed in a strong solution of zinc chloride with plates of zinc pressed closely against either

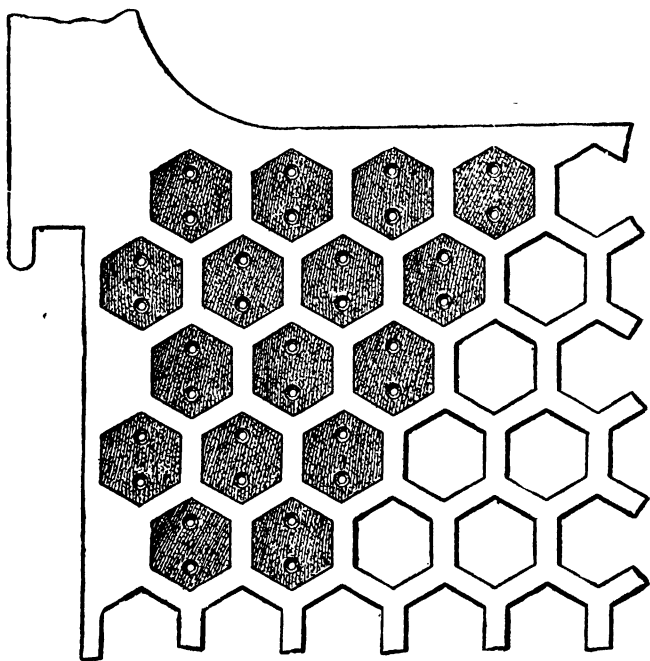


FIG. 192.—“Chloride” Negative.

side of them. The zinc combines with the chlorine to form zinc chloride, which dissolves up, and metallic lead remains. When this action is completed, the plates are removed to pure water and subjected to a prolonged washing, and after that are set up as negatives in very dilute sulphuric acid and a strong current passed through them. This “hydrogen bath” eliminates the last traces of chlorine from the active materials, and the plates are then ready for use.

For several years the positives used to be prepared in just the same way as the negatives, with the addition of a final reversal process, but it was found that lead peroxide obtained from lead chloride was not altogether satisfactory, and an entirely different plate has now been substituted, in which the active material is electro-chemically formed from metallic lead. This plate, termed by the company their "R" type, is a "plugged" electrode, and some account of it will be

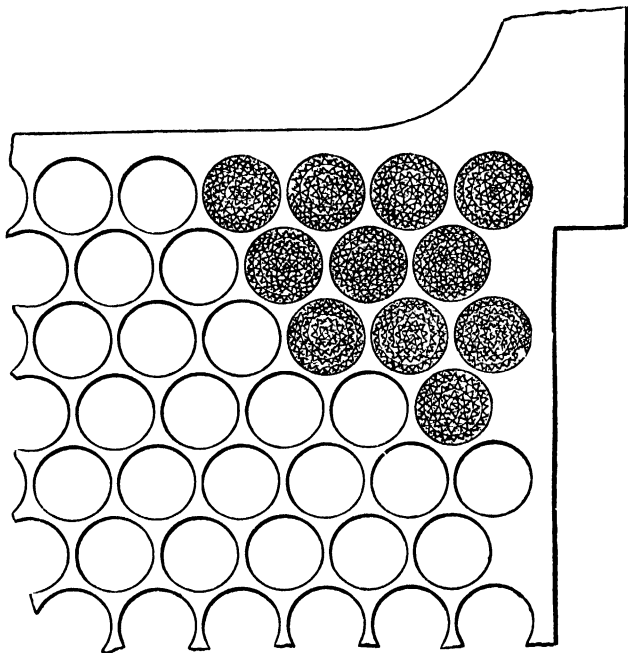


FIG. 193.—"Chloride" Positive.

found on page 82. A tape or strip of pure lead is passed through rollers, which gimp or emboss it with deep grooves and ridges, and cut it off into definite lengths. Each length is then rolled up by another machine into a circular pellet, and these pellets are put into round holes in a stout grid of antimonial lead which has been cast under pressure similarly to the negative supports. Finally, the electrode is placed in a hydraulic press in order to compress the pellets and force

each one into thorough contact with the support, and it is then ready to be formed. Fig. 193 shows a portion of standard "R" type plate.

The plates are mounted in the boxes by side lugs resting upon two upright glass slabs—a method common enough now, but which was first brought into general use in this country with Chloride cells. Three chief sizes of plates are manufactured: the "R" type, for ordinary use; the "CR" type, for central station work; and the "LR" type, for launch cells and other purposes where a smaller plate than the "R" type is necessary. Besides these, there are "PR" and "P₂R" plates for portable batteries and other special purposes. The outputs and charging rates per positive plate of the three principal sizes are given below:—

Type of Cell.	Output at Rate of Discharge in Hours.				Charging Rate.	
	1	3	6	9	Maximum.	Normal.
CR	66	97	119	132	33	18
R	30	44	54	60	15	8
LR	20	30	36	40	10	5

"Tudor" Accumulator.

It is only within comparatively recent years that these cells have been manufactured in this country by the Tudor Accumulator Co. at Dukinfield, but their original makers, the Accumulatoren-Fabrik Aktien-Gesellschaft, of Hagen, Westphalia, have been in existence from a much earlier period. From time to time the design of the electrodes has been considerably modified, but in nearly every case the positive support has remained of the ribbed and grooved type. At first it used to be slightly formed and then pasted, but now the whole of the active material is produced from the support by electro-chemical formation.

Fig. 194 shows a portion of a modern Tudor positive. It consists of a central web of metal covered on either side with a large number of thin vertical ribs, strengthened at frequent intervals by horizontal ribs slightly sunk below the surface. The subdivision of the metal and the increase of nominal surface is probably carried to the

utmost limit possible with a cast support. The plates are $\frac{1}{2}$ in. thick and have an actual surface nearly ten times their nominal surface, or twenty times if the comparison is made with one side only. This certainly constitutes a remarkable achievement in casting work, and its accomplishment requires elaborate and expensive moulds. Each half of a mould consists of a rectangular cast-iron frame in which are held a number of gun-metal racks, 15mm. wide, cut with very fine teeth, and a slight space is left

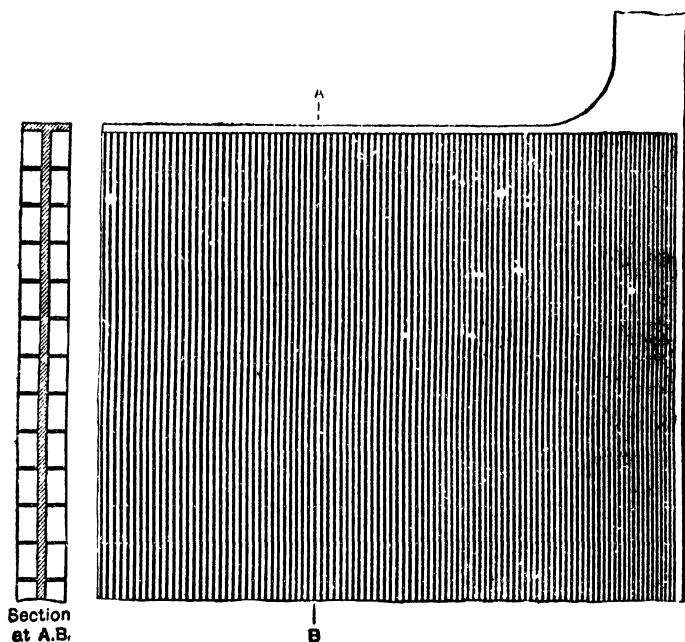


FIG. 194.—"Tudor" Positive.

between each rack corresponding to a horizontal rib on the plate. The ribs are as little tapered as possible, in order to avoid sharp edges at the surface, which would soon wear away.

The positives are formed in dilute sulphuric acid only, by a modification of the Planté process, which occupies about six weeks of continuous treatment. At first they are alternately charged and left on open circuit, but afterwards they are repeatedly charged and discharged at a current rate which

increases as the formation proceeds. When a sufficient capacity is obtained the plates merely have to be removed from the electrolyte and allowed to dry.

A portion of a negative support is illustrated in Fig. 195. It is a through grid with long narrow cells whose walls are of the usual tapering or diamond cross-section. Before pasting, the supports are charged as positives with a heavy

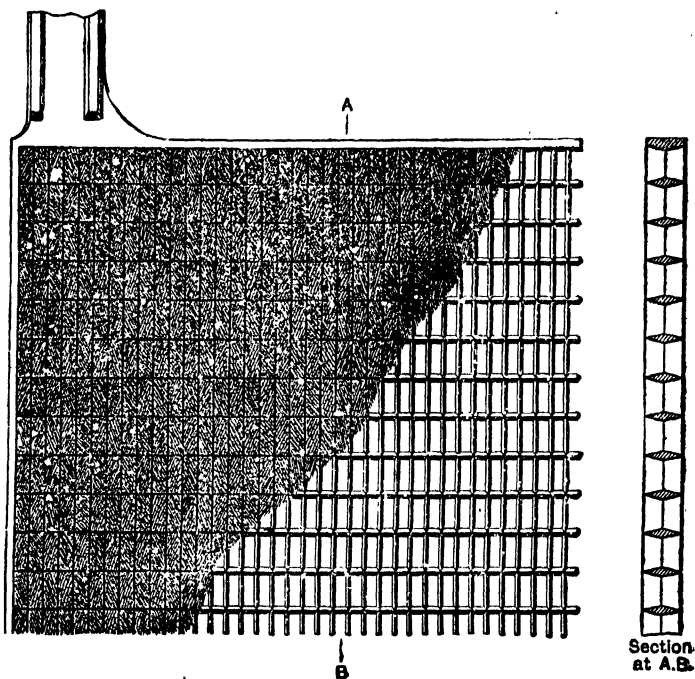


FIG. 195.—"Tudor" Negative.

current for a few minutes in order to clean and prepare their surfaces. The negative electrodes are usually sent out with their active material unformed. If it has been reduced to spongy lead in the usual way, it oxidises on drying in the air, and, when again set up in the electrolyte, sulphates so rapidly that the time occupied in the first charge after erection is very little less than if the plates had not undergone formation at all. On the other hand, the formed material has a

tendency to shrink away from its support when dry, and is more liable to scale and blister afterwards.

The Tudor Accumulator Co. make three standard sizes of plates: an "E" size, 7in. wide by 14in. deep; a "F" size, 14in. wide by 12in. deep; and a "G" size, which was formerly obtained by mounting two "F" type plates in an outer frame, but the difficulties of casting a single plate of equivalent size and capacity have now been overcome. Each size of plate is used to construct cells of two types, "L" and "H," which

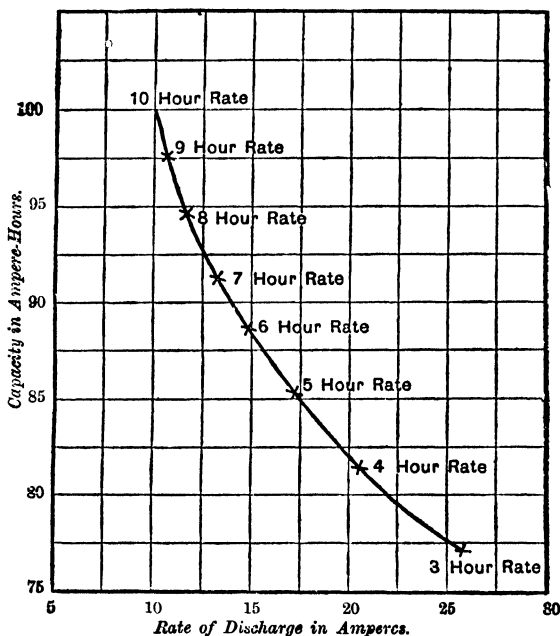


FIG. 196.—Percentage Variation of Output with Discharge Rate of "L" Types of Tudor Cells.

differ in the amount of formation of their positives, but are otherwise identical. The "L" type is most suitable for long discharges at comparatively low rates, such as are required in private installations or for the light loads of a central station. The "H" type has less capacity, but can be discharged and recharged at much higher rates, and is specially suited for taking up the variations of a load—either the comparatively

steady peaks of a lighting station or the rapidly fluctuating peaks of a traction or motor load. A "D" size of plate, $9\frac{3}{4}$ in. by $9\frac{3}{4}$ in., is also manufactured for replating boxes whose shape is unsuited to take those of the standard types.

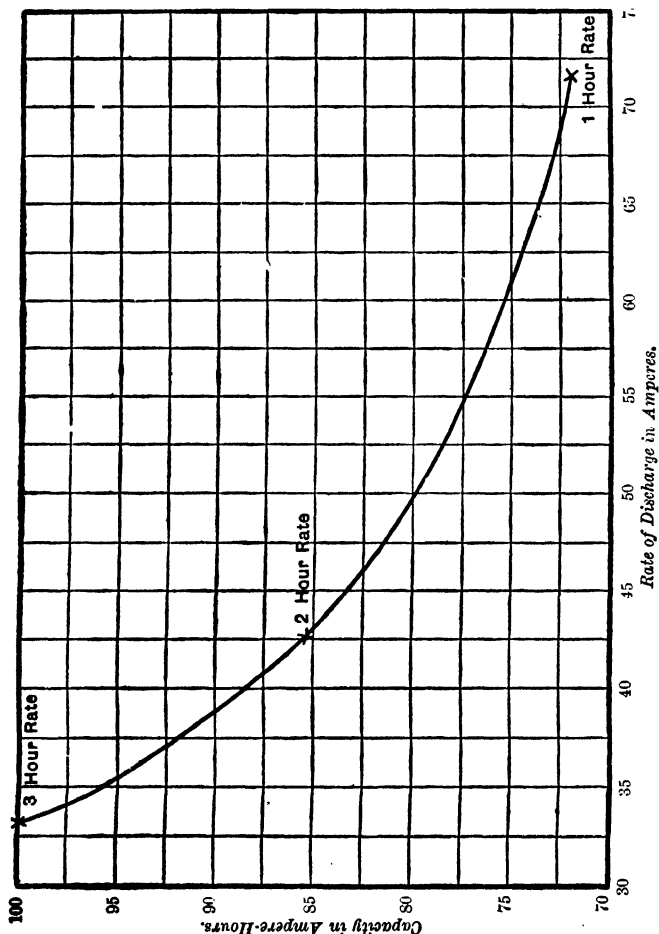


FIG. 197.—Percentage Variation of Output with Discharge Rate of "H" types of Tudor Cells.

The electrodes are mounted by hanging them from the sides of the containing-box when the latter is of glass, but if it is of lead or lead-lined wood, they are suspended on glass slabs which project above the surface of the electrolyte. A free space of 4 in. is left at the bottom of cells of the "E" or

"F" type, and of 8 in. in the "G" type, so that they need only be cleaned out at long intervals. The plates are

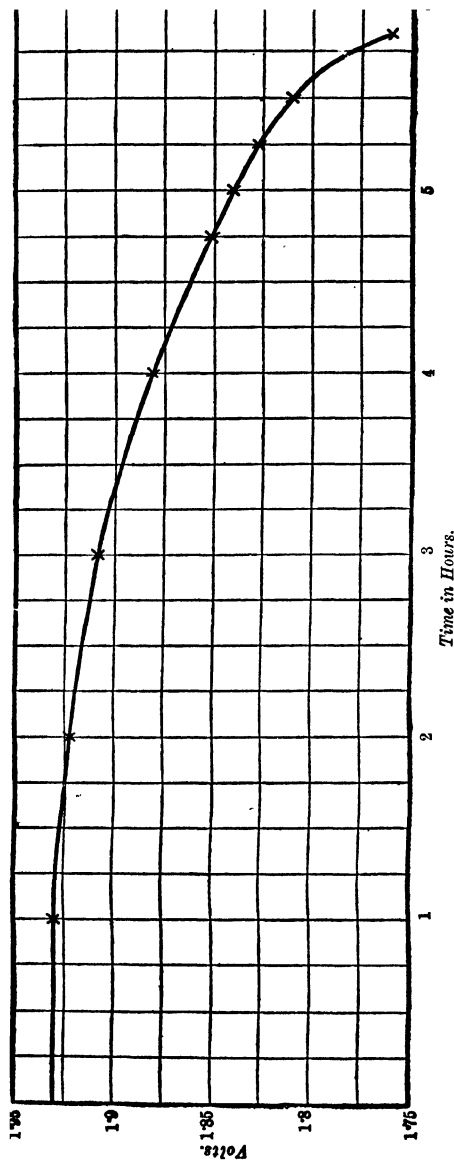


FIG. 198.—Curve of Discharge P.D. of "L" Type Tudor Cell.

separated by $\frac{1}{2}$ in. glass tubes held upright by guide pieces cast on the lugs of the negative plates (see Fig. 195).

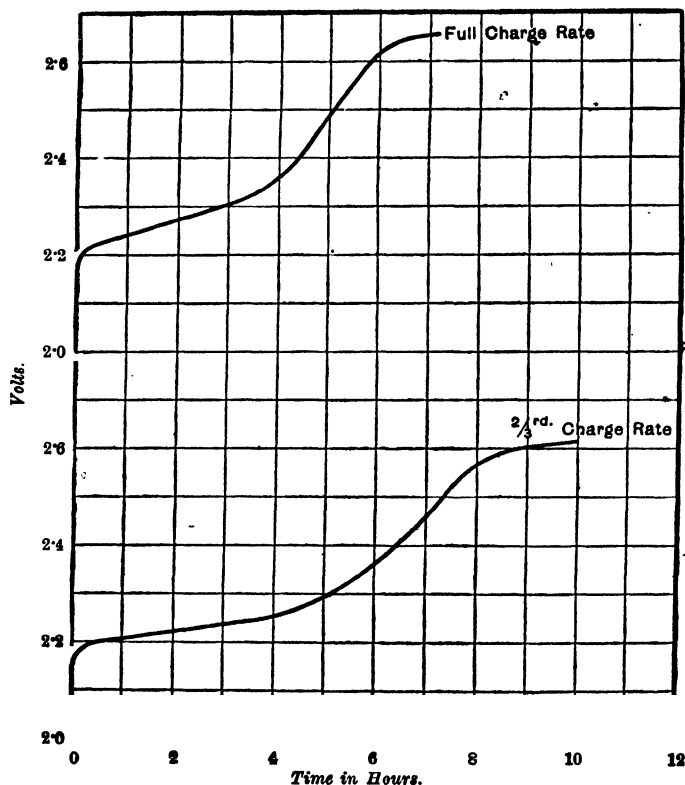


Fig. 199.—Curves of Recharge P.D. of "L" Type Tudor Cell.

The following table gives the outputs and maximum charging rate per positive plate for the various standard types of Tudor cells. Figs. 196 and 197 show the percentage

Type of Cell.	Output at Rate of Discharge in Hours.					Maximum Charging Rate.
	1	2	3	5	10	
H E	35	40	45	15
L E	48	55	60	10
H F	70	80	90	30
L F	99	110	125	20
H G	140	160	180	60
L G	198	220	250	40

variations of output at different discharge rates of the "L" and "H" types respectively; Fig. 198 the curve of P.D. of the "L" type when discharging at a five-hour rate; and Fig. 199 the curves of recharge P.D. of the "L" type when recharging at maximum and two-third maximum rate respectively.

"P. and G." Accumulator.

These cells are made by Messrs. Pritchetts and Gold, of Feltham, and all the electrodes in the ordinary types intended for stationary and general use are of the formed

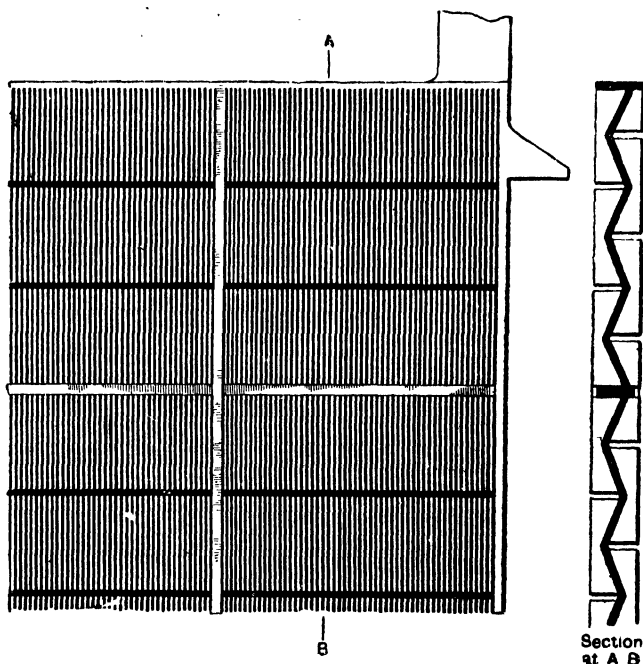


FIG. 200.—"P. and G." Positive.

variety. The firm are the sole licencees in this country for the manufacture of plates according to the patents of Dr. Lehmann, of the Berliner Accumulatoren- und Elektricitäts-Gesellschaft, and they are also worked in France by Messrs. Geoffroy and Delore, of Clichy, under the name of the "Omega" accumulator, and in Belgium by La Société l'Electrique of Brussels. Fig. 200 gives a face view and

cross-section of a part of one of the standard P. and G. positives. Its special construction consists in the substitution of a zig-zag core in place of the usual straight one, and in the subdivision of the vertical ribs into a number of short sections or flaps by means of numerous horizontal grooves penetrating right down to the core. The perspective view of a small portion of an electrode shown in Fig. 201 will make the arrangement quite clear. The object of this design is to make every allowance for the expansion of the support in all directions, and thereby to reduce the liability to buckling and distortion to a minimum. It will be observed that the grooves occur where the core is furthest from the surface, and the two sets on either side of the plate are

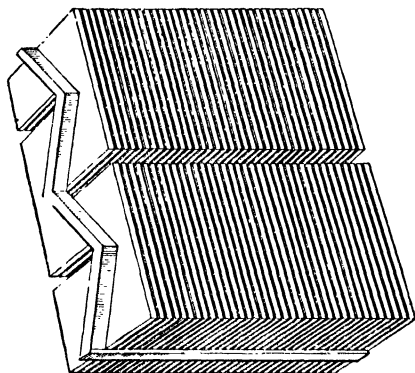


FIG. 201.—Detail of "P. and G." Positives.

staggered relatively to each other. The support is divided into nine equal panels by four solid ribs, two vertical and two horizontal, which are slightly countersunk below the general level of the electrode and cross it from side to side.

As there is no further production of active material by local action at the negative electrode once it has been formed, and consequently no growth of the support, the latter is a horizontally-ribbed plate of the ordinary kind, as shown in Fig. 202, and it is merely provided with a straight core. The formation of the electrodes is effected by a process which only occupies about three days for completion, and yet avoids the use of chemicals that might injuriously affect their after-life.

The standard size of plate is about $9\frac{1}{2}$ in. by 9 in. The positive are $\frac{1}{2}$ in. thick and weigh about $11\frac{1}{2}$ lb. each; the negatives $\frac{3}{8}$ in. thick and weigh $8\frac{1}{2}$ lb. The output per positive is 65 ampere-hours at a nine-hour rate, or 30 ampere-hours at a one-hour rate. The weight of the plates relatively to their output is considerably above the average in order to propor-

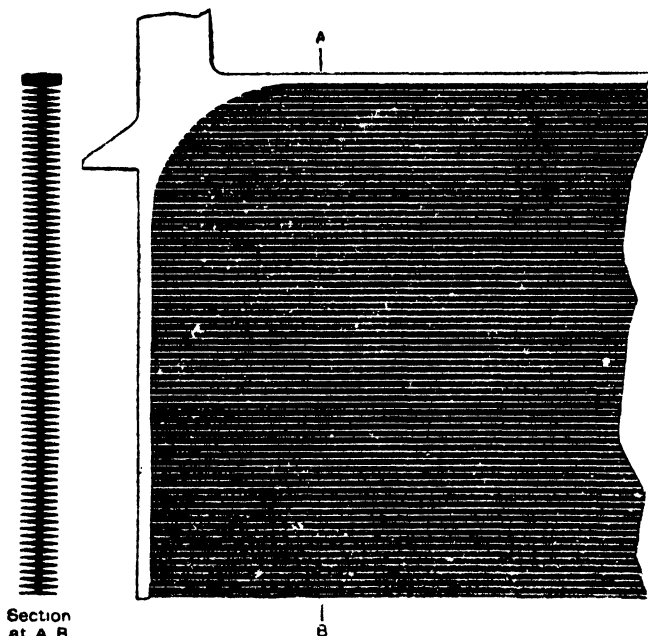


FIG. 202.—“P. and G.” Negative.

tionately increase their durability. For automobile purposes, where weight cannot be ignored, a special type of electrode is made.

“Hart” Accumulator.

The cells of the Hart Accumulator Co., of Stratford, are fitted with positive and negative plates all of the pasted type. Fig. 203 shows the nature of the negative supports. They consist of an outer frame, a series of stout diagonal bars about 1 in. apart, and a number of slighter and more closely spaced horizontal ribs, all of the full thickness of the electrode. Between and parallel to the diagonal bars

are other slight ribs only about half the thickness of the plate and appearing alternately on either surface. The general effect is that of a number of horizontal strips of light grid work situated first on one side and then on the other. A special feature of the support is the rows of projections which stand up from the horizontal ribs when cast, but are afterwards turned over flush with the surfaces and constitute a series of lips to help keep the active material in its place.

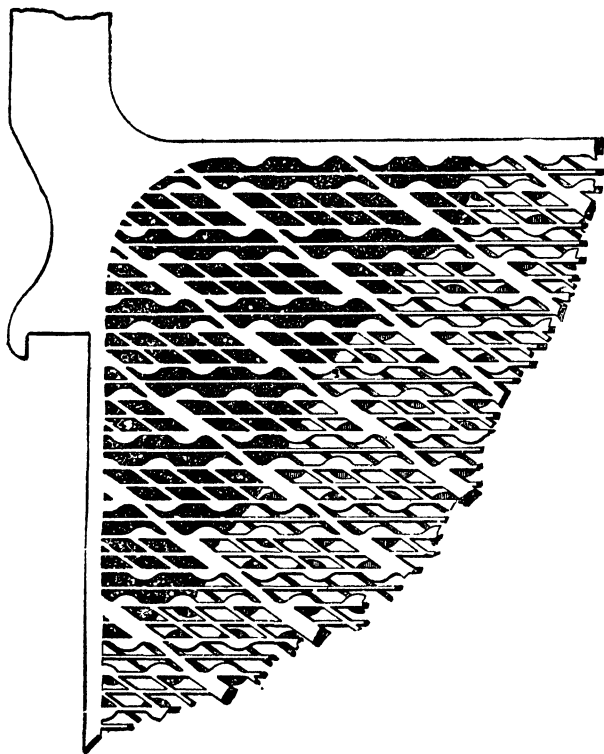


FIG. 203.—“Hart” Negative.

The positive supports used to be of similar design to the negatives, but a somewhat heavier and stronger kind has now been substituted. It is a horizontally-ribbed plate with a central web of solid metal further stiffened by some vertical ribs and two diagonal ones crossing from corner to corner

(see Fig. 204). The horizontal ribs are cast at right angles to the core, and are then set up by a special rolling process so as to provide incline shelves on which the active material rests without fear of its falling out.

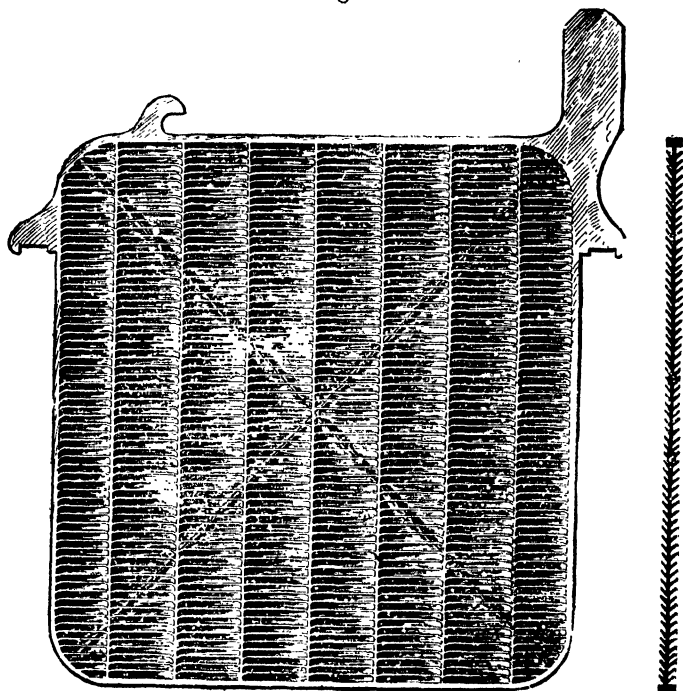


FIG. 204.—“Hart” Positive.

The company supply four chief types of cell, namely, the “lighting,” “traction,” “central station” and “portable” or “S” type. Their outputs and charging rates per positive plate are as follows :—

Type of Cell.	Output at Rate of Discharge in Hours.						Charging Rate.	
	1	2	4	5	7	9	Normal.	Maximum.
Lighting	40	45.5	49.5	5	...
Traction	20	24.5	27	2.5	...
Central station...	40	60	80	100	12	20
Portable (S)	9	...	0.5	1.3

The electrodes are hung on glass slabs and separated by glass tubes in the usual way. Fig. 205 shows the special

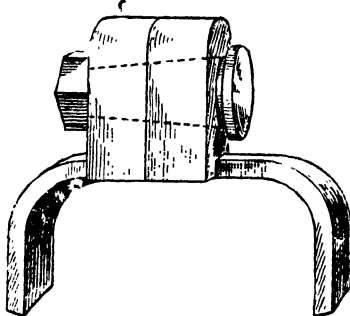


FIG. 205.—“Hart” Battery Connection.

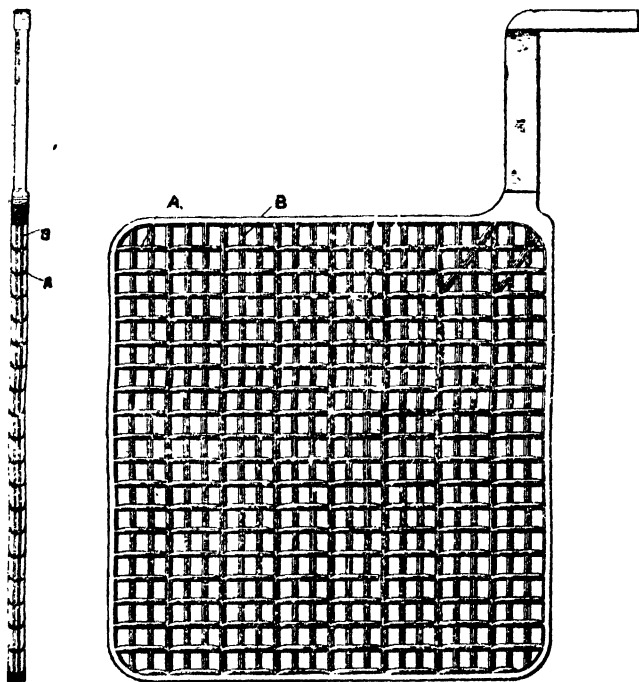


FIG. 206.—“Hart” Light Traction Grid.

device used for connecting the cells together. The main bar to which each section of plates is joined terminates in a lug

having a smooth vertical face and a conical hole through its centre. The faces of two adjacent lugs are brought together and clamped up by means of a taper bolt passing through the holes and a nut, both of some lead alloy. In this way an entirely non-corrosive connection is provided, partly direct from lug to lug and partly through the bolt itself.

Recently a special type of traction cell, giving an output of about 4 ampere-hours per pound total at a five-hour rate, has been added to the company's manufactures. Its negative electrodes are of similar construction to the other types, but the positive support is of the kind shown in Fig. 206. The horizontal bars or shelves project beyond the general level of the plate when cast, but they are afterwards turned up by passing through rollers, so as to form shallow troughs. The positives are wrapped in a thin porous silicated cloth when mounted in the cell, and perforated ebonite sheets with ribs are used as separators.

"A. B. P." Accumulator.

These cells are manufactured by Ashmore, Benson, Pease & Co., of Stockton-on-Tees, who were at one time the makers in this country of the "Invicta" accumulator, a type of cell of French design. Their "Stockton" types, which are those intended for general use and central station work, contain formed positives and pasted negatives made in one of two sizes—14in. by 14in., or 10½in. by 9in. Fig. 207 shows a portion of a positive support. It is a cast ribbed plate of the "through" type, $\frac{5}{16}$ in. thick, and, in lieu of a central web of metal, is provided with stout horizontal and vertical strengthening bars at frequent intervals. A special feature of the plate is that these bars are covered with shallow grooves, which form a continuation of the spaces between the small horizontal ribs. By this device the smooth vertical surfaces of considerable area, from which large flakes of active material might break away and set up short-circuits with the neighbouring electrodes, are entirely avoided.

A portion of the negative support is shown in Fig. 208. It is a grid of the double-lattice type cast in pure soft lead.

Substantially it consists of a number of horizontal bars of triangular cross-section, with the apex turned inwards, set alternately at either surface of the support. The bars, which are only about one-third as deep as the total thickness of the electrode, are linked together by a series of horizontal cross-ties zig-zagging diagonally through the plate from side to side and bar to bar. The result is a light open-work structure, in which the whole of the active material forms one continuous and united mass.

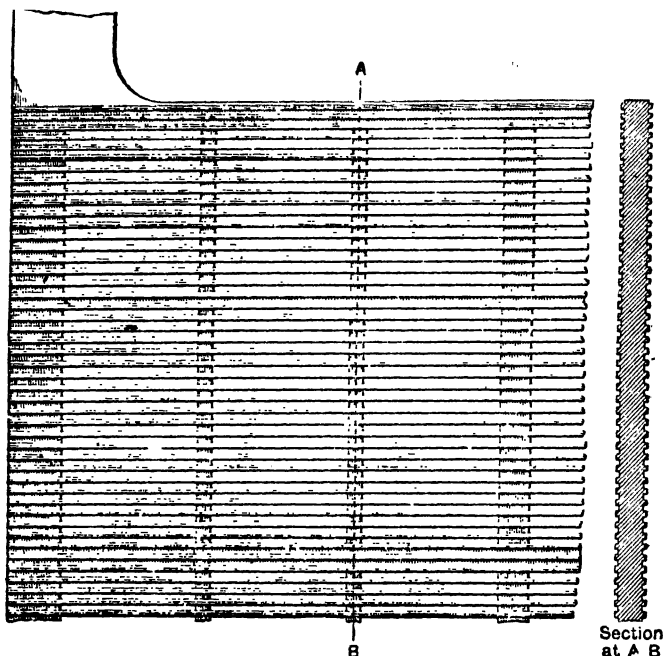


FIG. 207.—“A. B. P.” Positive.

The method of mounting the electrodes in the cell is illustrated in Fig. 209. They are hung on the edges of the box; separated by glass tubes; and the whole section is tied together by two outside frames of lead-antimony alloy and cross-connecting strips. The shape and position of these frames may be seen from the figure.

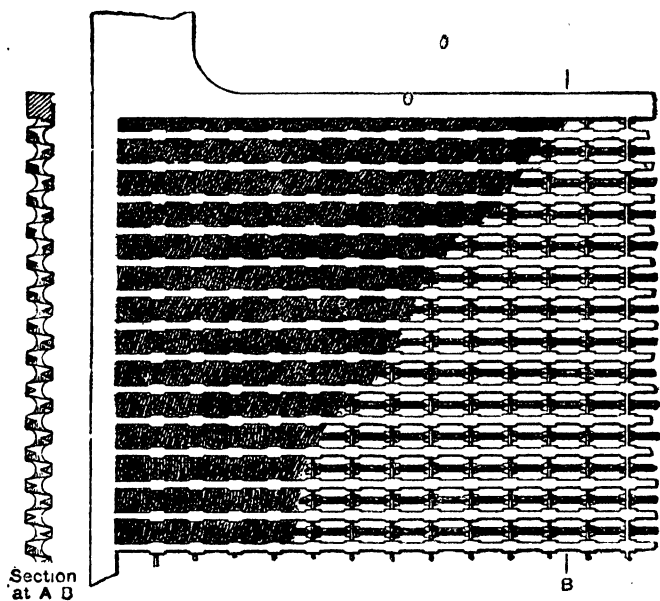


FIG. 208.—“A.B.P.” Negative.

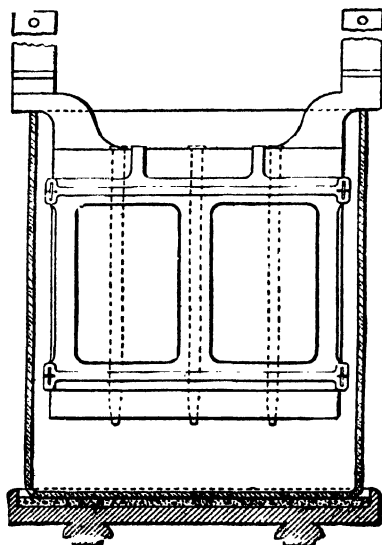


FIG. 209.—“A.B.P.” Cell.

"F. T. L." Accumulator.

The British Power, Traction and Lighting Co., of York, are the makers of these cells, which were at one time known as the "Victoria" accumulator. Both the positive and negative electrodes are of the pasted type and of similar design, but differ in thickness. Fig. 210 shows a portion of the double interlocking grid support. It is constructed of two thin grids with square cells and tapering cell walls, fitted

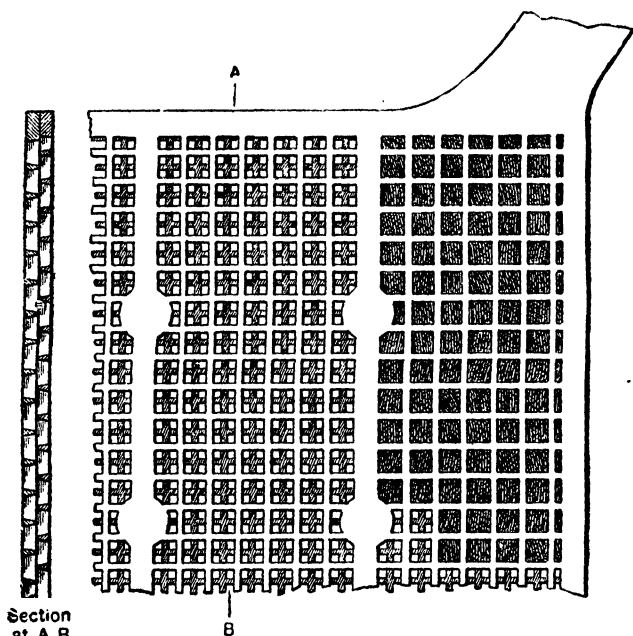


FIG. 210.—"P. T. L." Grid.

together by means of projecting pins on the one grid passing into corresponding holes in the other. The two grids are then burned together all round their edges and where the ends of the pins project through to the opposite surface. The two sets of grid-work are displaced relatively to each other by the width of half a square in both directions, so that the points of junction of the bars on one side come over the centres of the apertures on the other side. The method

adopted for connecting the cells together without the use of any metal that will be attacked by the acid spray is shown in Fig. 211. A rectangular collar^o of lead alloy is slipped over the upturned ends of the two main bars, and then a wedge of similar metal is firmly driven in between them.

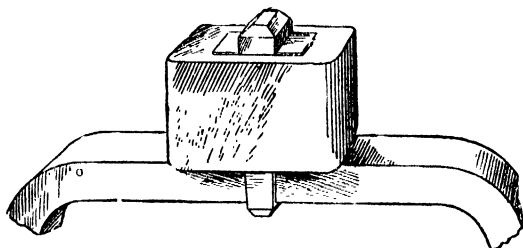


FIG. 211.—“P. T. L.” Cell Connection.

“Laitner” Accumulator.

Two quite distinct types of these cells are manufactured by Accumulator Industries Limited, of Woking. The one intended for central station work and general use contains formed positives and pasted negatives. On casual inspection, the positive support appears to be an ordinary grooved plate, with solid metal backing; but in reality the metal below the surface is distributed in a cell-like structure, which allows the circulation of the electrolyte completely through the plate, and yet gives the strength and conductivity of the usual central core. This construction necessitates a rather complicated mould, and the supports are cast in a special machine on the “Francke” system. The formation is effected without the use of nitric acid or other dangerous substances in the electrolyte.

The negative support is of the double-lattice type, with undercut ribs, only half the depth of the electrode, spaced alternately on either surface, and strengthened at intervals by diagonal bars of the full thickness. Perfect continuity of the active material throughout the electrode is thereby provided for, and the possibility of its losing contact with the support by shrinkage is eliminated.

The electrodes are generally sent out detached for connecting up to main bars common to adjacent cells, according

to the accepted central station practice. On first mounting the battery they are, however, merely clamped down by bolts of hard lead alloy, which screw into the bars at the proper distances apart; then, after the first charge is completed, they are permanently burned into position by an electric arc actuated with current from the cells themselves.

Fig. 212 gives a series of curves of P.D. obtained from a stationary type 9-plate cell discharging at different rates. The discharges were taken on consecutive days, commencing at the slowest rate, and the cell was well charged between each. When discharging in $1\frac{1}{2}$ hours the output is still two-thirds of what it was at an 11-hour rate—a very good record. The positive electrodes in the cell weighed 7lb. 9oz. each, and were about 8in. by 10in. by 0.4in. thick; the negatives weighed 6lb. 2oz. each, and were about 0.25in. thick.

The second make of cell is termed the "light traction" type, and is designed for use in electrically propelled vehicles or wherever a reduction of weight is the chief consideration. In this case all the electrodes are of the pasted variety and similar in design, except for a difference of thickness between the positives and negatives. Each support consists of a central sheet of thin perforated lead, with an undercut frame cast round it. The paste is filled in flush with the edges of the frame on both sides. All the details of the cell being arranged with a view to economisation of bulk and weight, the electrodes are spaced close together, with perforated sheet ebonite separators; and a strong acid electrolyte, of a specific gravity up to 1.3, is employed. It is this make of cell that was fitted in the Krieger car "Powerful," which made a 95-mile run on one charge in 1901, and also in several other cars that have covered long distances.

The light traction plates are made in several different sizes, and the proportions of the plates themselves—such as their thickness or that of the central perforated sheet—are also varied, so that a considerable range of outputs for weight from 10 to 25 watt-hours per pound of complete cell can be obtained, according to the work the cell is required to do and the life expected. Fig. 213 shows the discharge P.D. of two 200 ampere-hour cells. Curve A is that of a cell weighing 26.5lb. and discharging at 22 amperes; curve B

M.F.

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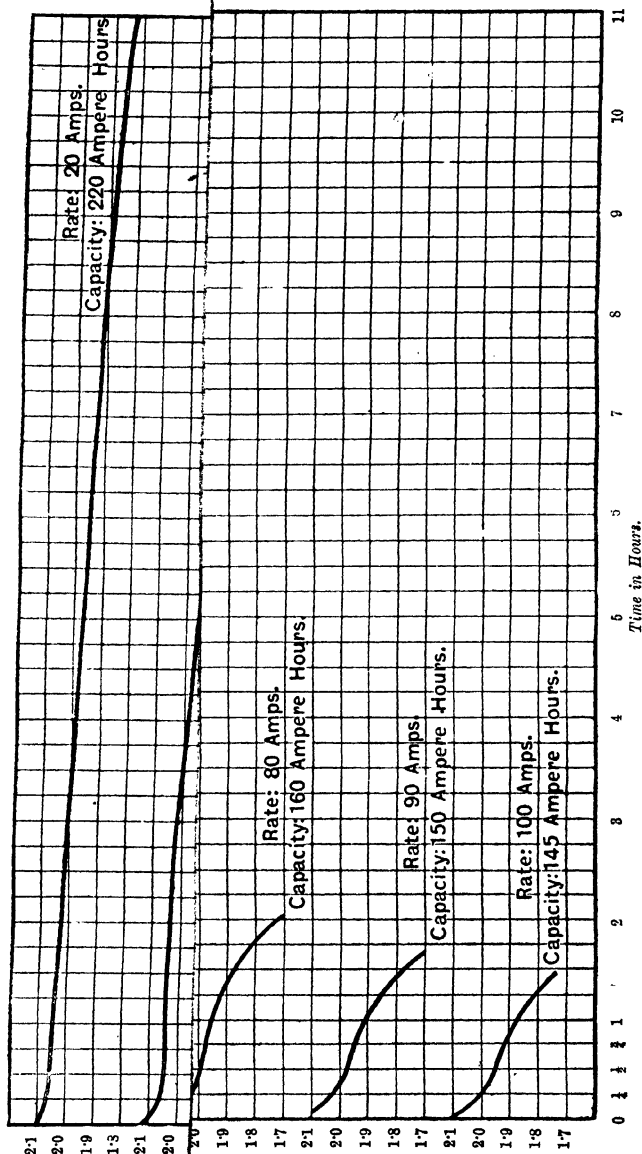


FIG. 212.—Curves of Discharge P.D. of "Leitner" cell discharging at different rates.

to the accepted central station practice. On first mounting the battery they are, however, merely clamped down by bolts of hard lead alloy, which screw into the bars at the proper distances apart; then, after the first charge is completed, they are permanently burned into position by an electric arc actuated with current from the cells themselves.

Fig. 212 gives a series of curves of P.D. obtained from a stationary type 9-plate cell discharging at different rates. The discharges were taken on consecutive days, commencing at the slowest rate, and the cell was well charged between each. When discharging in $1\frac{1}{2}$ hours the output is still two-thirds of what it was at an 11-hour rate—a very good record. The positive electrodes in the cell weighed 7lb. 9oz. each, and were about 8in. by 10in. by 0.4in. thick; the negatives weighed 6lb. 2oz. each, and were about 0.25in. thick.

The second make of cell is termed the "light traction" type, and is designed for use in electrically propelled vehicles or wherever a reduction of weight is the chief consideration. In this case all the electrodes are of the pasted variety and similar in design, except for a difference of thickness between the positives and negatives. Each support consists of a central sheet of thin perforated lead, with an undercut frame cast round it. The paste is filled in flush with the edges of the frame on both sides. All the details of the cell being arranged with a view to economisation of bulk and weight, the electrodes are spaced close together, with perforated sheet ebonite separators; and a strong acid electrolyte, of a specific gravity up to 1.3, is employed. It is this make of cell that was fitted in the Krieger car "Powerful," which made a 95-mile run on one charge in 1901, and also in several other cars that have covered long distances.

The light traction plates are made in several different sizes, and the proportions of the plates themselves—such as their thickness or that of the central perforated sheet—are also varied, so that a considerable range of outputs for weight from 10 to 25 watt-hours per pound of complete cell can be obtained, according to the work the cell is required to do and the life expected. Fig. 213 shows the discharge P.D. of two 200 ampere-hour cells. Curve A is that of a cell weighing 26.5lb. and discharging at 22 amperes; curve B

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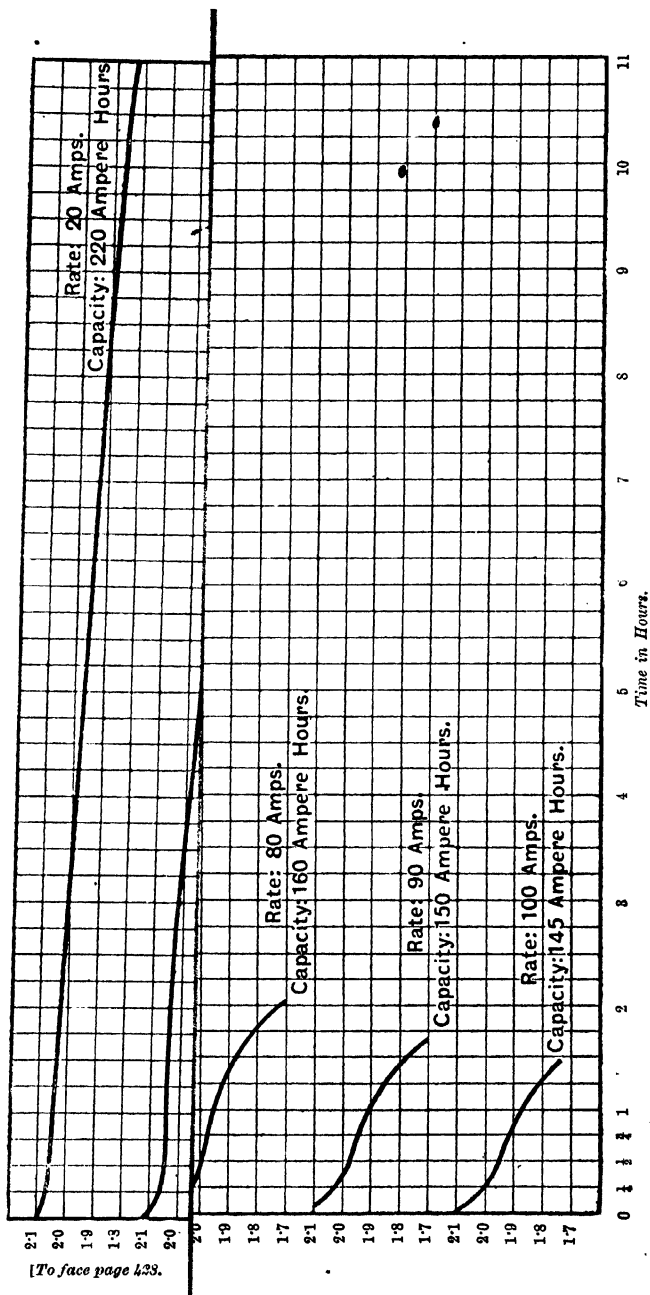


Fig. 212.--Curves of Discharge P.D. of "Leitner" cell discharging at different rates.

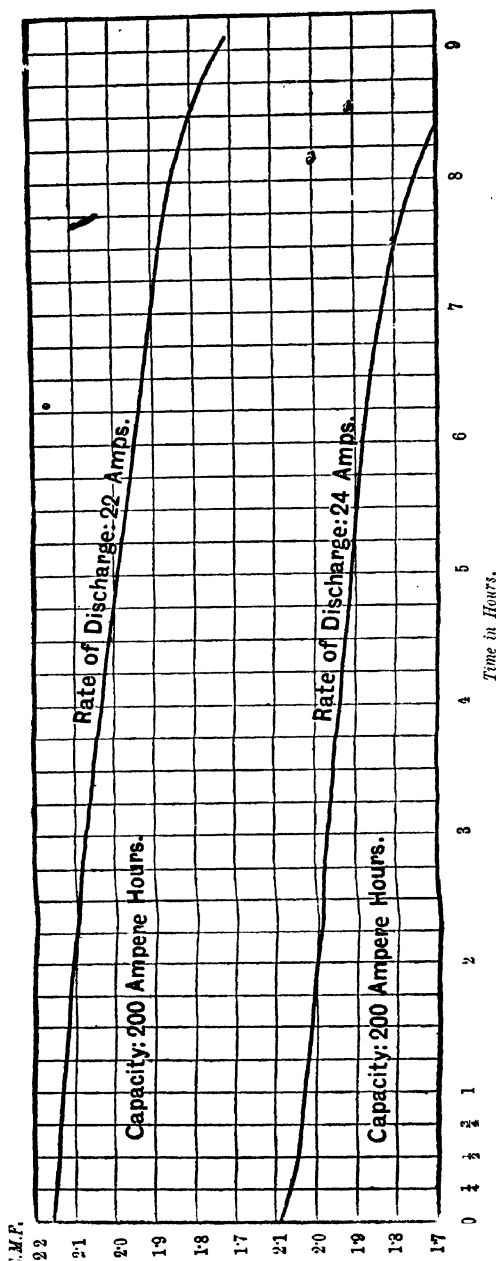


FIG. 213.—Curves of Discharge P.D. of "Leitner" Cells of the "Light Traction" Type.

that of a cell weighing 27·25lb. and discharging at 24 amperes. The output in these cases is therefore about $7\frac{1}{2}$ ampere-hours per pound of complete cell.

“Lithanode” Accumulator.

The word “lithanode” was first used by Mr. D. FitzGerald in 1884 (when local action between the lead peroxide and the metallic lead of the support was supposed to be the bane of lead cells) to describe a form of positive-active material which possessed sufficient porosity, conductivity, and coherence to be made up into electrodes, either without any support at all, or with merely a rudimentary one of platinum or other unoxidisable material which should convey the current to the external circuit. Since then, the control and limitation of local action has, on the one hand, become better understood, while, on the other, it is now recognised that, in general, the correct principle of design is to increase rather than decrease the area of contact surface between the support and the active material, and that, even in special cases where reduction of weight is of first importance, the suppression of the support cannot be carried too far. Some of FitzGerald’s processes of manufacture (already mentioned on page 45) and the types of electrode which have been evolved in connection with them, are still made use of by Longstreth’s Limited, who construct a large variety of cells, chiefly in the smaller sizes, actuating cauteries and medical lamps, auto-car ignitions, X-ray apparatus, and for many other similar purposes. One special type of cell employed for cable testing has to be frequently discharged almost on short-circuit for several minutes together. It is made in different sizes up to a capacity of about 200 ampere-hours. The design of the negative electrodes varies according to the use to which they are to be put. A lead wire meshing cast in a slight frame is a frequent one, and, in certain instances, a copper gauze well protected with a coating of lead is found to answer satisfactorily. The positive electrodes contain large pellets of active material, which are moulded separately and formed, and then have a stout metal frame cast round a suitable number of them. An oblong pellet about 2in. by $\frac{3}{4}$ in. is a usual size and shape, and it has bevelled edges so that it may key into its support.

"Monobloc" Accumulator.

Messrs. Drake and Gorham are the sole agents for the Monobloc Accumulator Syndicate, and their cells are manufactured in this country by the D.P. Battery Co. The cells

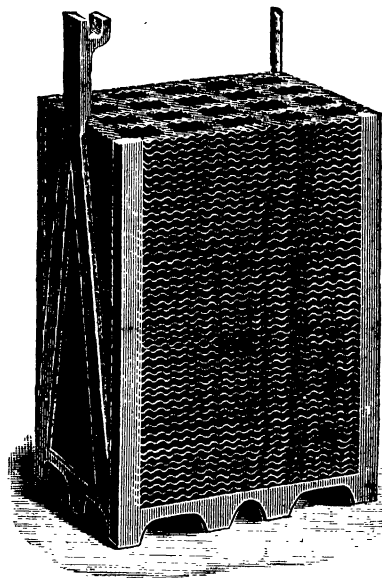


FIG. 214.—"Monobloc" Positive.

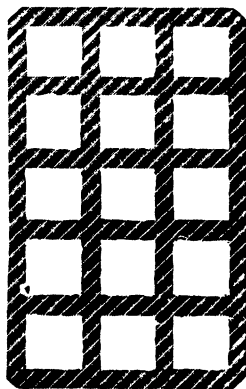


FIG. 215.—Single sheet of "Monobloc" Positive.

are more especially intended for traction work or other uses where the requirements are somewhat similar, and their design, which is novel and unusual, is due to E. Julien. Whatever the size of the cell, the positive electrode consists of a single block—hence the name—of sheets of corrugated lead, piled one upon the other and burned together and to a connecting frame at the corners (*see* Fig. 214). All the sheets are similarly perforated (*see* Fig. 215) so as to provide a number of deep square apertures in which the negative electrodes are

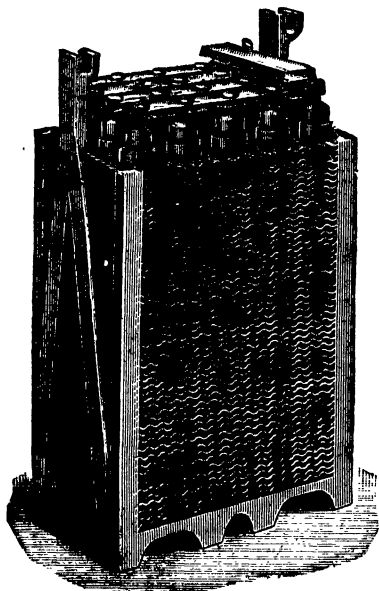


FIG. 216.—"Monobloc" Section.

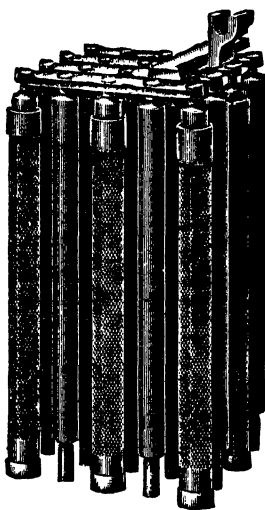


FIG. 217.—"Monobloc" Negative.

placed, as shown in Fig. 216. The negatives are long narrow rods composed of a central conducting core surrounded with active material, and kept from contact with the positive by outer sheaths of insulating material. Their general construction is better seen in Fig. 217, where some of the rods are illustrated with the separators removed so as to expose the insulating pegs fixed to the bottom of the rods, and on which they stand. The active material of the positive is Planté-formed; that of the negatives of the pasted type.

"Allan" Accumulator.

These cells are manufactured by the P. and R. Storage Battery Co., of Ashted. Their electrodes are all of the pasted type, the support consisting of a double lattice grid of the kind shown in Fig. 218. The cross-bars, forming the diamond-shaped apertures, are of triangular section, and, by the use of special moulds, are cast with their broadest part on

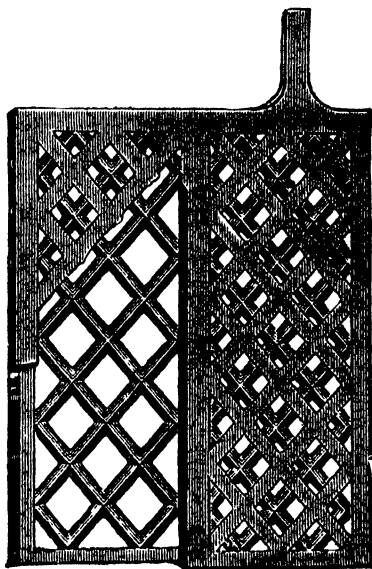


FIG. 218.—"Allan" Electrode.

the outside and the taper inwards. Each lattice is about $\frac{1}{8}$ in. thick and between them there is a clear space of about $\frac{3}{8}$ in., making the total thickness of the plate about $\frac{5}{8}$ in. The two lattices are united by bars at the top and sides, the latter being perforated to give a further access of electrolyte to the active material; while supports of the size illustrated—9 in. by 7 in.—are further tied together and strengthened by a vertical bar passing down their centre.

"Armoured" Accumulator.

The P. and R. Storage Battery Co. also make the plates of these cells for Messrs. Peto and Radford. Their construction is somewhat novel, as may be seen from Fig. 219. The electrode proper, is merely a light grid containing pastilles of active material about $\frac{1}{2}$ in. square, but this slides into a slight outer metallic case with open-work sides of bars arranged in

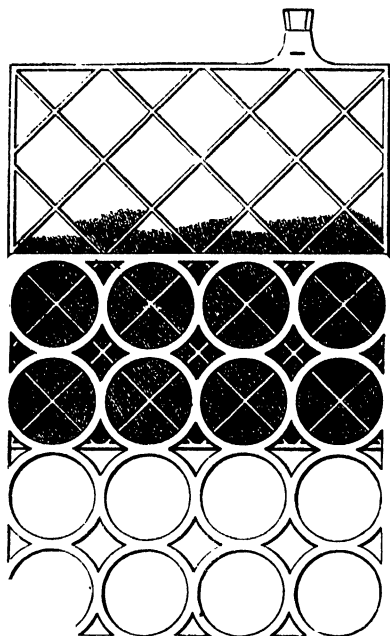


FIG. 219.—"Armoured" Electrode.

circles. These bars pass across the centres of the pastilles, and to further hold the active material in its place, a sheet of perforated ebonite is slipped between the electrode and its case on either side. In the figure, the electrode is shown partly withdrawn from the case and with its upper portion unpasted. The perforated sheets are omitted.

The electrodes are only made at present in a small size about 4 in. square, and specially intended for use in motor-car

ignition cells. Messrs. Peto and Radford are also the agents in England for the "Dinin" cells, which are employed for similar purposes.

"Marquand" Accumulator.

The speciality in the electrodes manufactured by the Marquand Accumulator Co., of Cardiff, is their method of formation. Plates of cast lead are covered on either side with powdered sulphur, closed up in iron boxes, and subjected in an oven to a temperature at which the sulphur and lead combine to form a sub-sulphide. After cooling, the plates undergo an electrolytic formation in dilute sulphuric acid in the usual way. The sulphur is removed either as hydrogen sulphide, H_2S , or by oxidation to a thionic acid; and a porous layer of lead or lead peroxide in intimate connection with the underlying and unaltered metallic lead is obtained.

"Gülcher" or "Woven Glass" Accumulator.

These cells are supplied by Messrs. H. W. Van Raden & Co., of Coventry. The electrodes are of the pasted type,

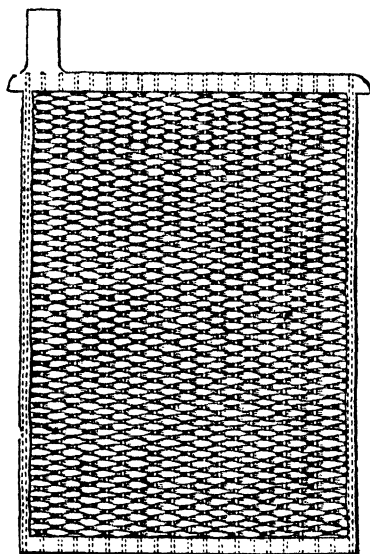


FIG. 220.—"Woven Glass" Electrode.

with supports consisting of a woven fabric of lead wires as warp and bundles of fine glass threads as weft cast up in a lead frame (see Fig. 220).

In the smaller cells these plates are used for both positives and negatives, but for traction cells and other purposes where heavy discharges are required a Planté-type positive has now been introduced. This is illustrated in Fig. 221. Short strips of lead tape, 0.3mm. thick and spaced 0.4mm. apart, are made up into packets and arranged in a suitable mould for the purpose of casting lead bars on to their ends

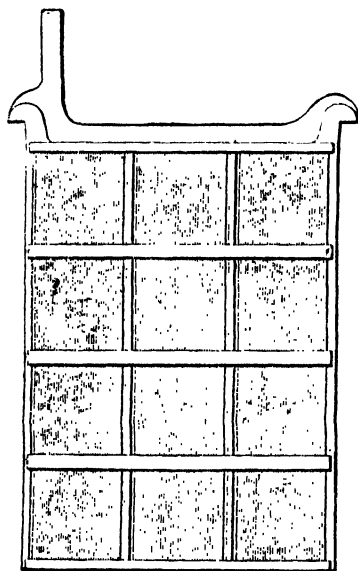


FIG. 221.—“Gülcher” Positive.

and uniting the several sets to form the panels of a single electrode. Spaces are left between the vertical bars and the strips, into which the latter can expand during formation and after use. The actual surface of the plate is about 15 times its nominal surface.

“Pollak” Accumulator.

These cells are manufactured in Germany, but are supplied in England by Messrs. W. C. Horne & Sons. Full particulars and illustrations of the design of the electrodes are given on page 452.

"Sherrin" or "Pope" Accumulator.

These cells attracted considerable attention a little time back on account of the good results they yielded in the accumulator competition organised by the Automobile Club de France in 1898, but they are not now being manufactured. The construction of the positive electrode is shown in Fig. 222. It is built up of a number of pasted rods, each composed of a helically-twisted hard lead core of H girder section, wound

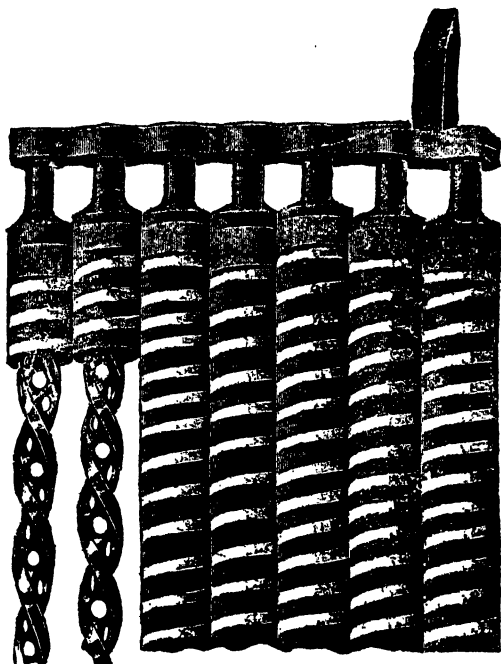


FIG. 222.—"Sherrin" Electrode.

with a spiral strip of ebonite and filled in flush with active material. The core is perforated at intervals. In the trials above mentioned, each finished rod was further overwound with thin perforated ebonite sheet. Some slightly different designs have already been illustrated on page 68, Figs 58 and 59.

The negative electrode was simply a pasted lead frame with an extremely slight conducting network passing through the interior of the active material.

"Still" or "Ideal" Accumulator.

These cells have been designed especially with a view to lightness for automobile work. Their electrodes are constructed from sheets of lead slit up into strips like the teeth of a comb, while at the same operation, the strips are twisted over at a right angle so that they form a series of horizontal shelves into which the active material is filled. They are, in fact, a very slight form of strip electrode with a single main conductor all in one piece. The shelves are prevented from separating by vertical rubber bands passing round the plate. The cells give an output of about $5\frac{1}{2}$ ampere-hours at a 5-hour rate.

"Rosenthal" or "National" Accumulator.

These cells are manufactured by Messrs. H. F. Joel & Co. especially for traction work and electric automobiles. Their electrode supports for pasting consist of a slight grid with rectangular apertures, approximately $\frac{3}{4}$ in. by $\frac{1}{2}$ in. The vertical diamond section bars are the full thickness of the plate, but the thin horizontal ones of circular section are entirely sunk below the surface of the active material. The output per pound of complete cell is as high as 6 ampere-hours at a 5-hour rate.

"Taipo" Accumulator.

These cells are made by the Taipo Accumulator Co., under the patents of J. G. Hathaway. The positive active material is held in shallow trays of porous earthenware, and two of them placed on either side of a central sheet of thin lead constitute an electrode. The faces of the porous plates have a corrugated form, so that when placed close up to the adjacent negatives they only contact with them in places, and a series of channels is left for the circulation of the electrolyte.

"Oppermann" Accumulator.

The chief speciality of this make consists in the method of preparing their active material with a view to obtaining great durability and high specific output. The lead oxide is first mixed to a dry mass with a solution of Trinidad bitumen in some suitable hydrocarbon; then made into a paste with dilute sulphuric acid and applied to light, thin grids in the usual way. The electrodes are placed very close together

with separators of corrugated, perforated sheet ebonite between them, and the section is held in position by one or two long ebonite bolts passing through the whole of the plates and clamping up with nuts on either side.

The cells are manufactured by Mr. Carl Oppermann, of Wynyatt-street, London, E.C., chiefly for use in electric automobiles, and a large output for weight can be obtained from them.

"Umpire" Accumulator.

The electrodes are of the sunk grid type, so that the support is entirely covered with active material except at the edges. Porous separators, ribbed on the side adjacent to the negative, are used between the plates, and the entire section is held together by rubber bands. Messrs. Sutherland and Marcuson are the makers.

AMERICAN CELLS.

Long after the lead accumulator had firmly established itself in this country and on the Continent of Europe, and was being largely employed in the various departments of electrical engineering, it still remained a practically negligible quantity in the United States. Many attempts had been made to develop it on a commercial scale, but they had only ended in a prolonged litigation for infringement of patent rights, out of which the owners of the Brush interests finally emerged triumphant; not apparently in a position to do very great things themselves, but having successfully fought or scared all rivals out of the field. As the fundamental Brush patent covering the use of ribbed and most other kinds of supports for formed electrodes did not expire till close on 1900, and the basic patent for pasted electrodes—filed at the same time as the other but delayed in the patent office for five years—only expired in 1903, the prospect was not very encouraging, but about 1895 things took a turn for the better.

American "Chloride" Accumulator.

The Electric Storage Battery Co., of Philadelphia, was founded in 1888 to work a number of patents relating to cells and electrodes whose active materials were prepared from cast lead chloride, a method which might not unreasonably

be supposed to lie outside the Brush and Faure claims; but when, after several years devoted to perfecting the design and manufacture of chloride cells, this position was disputed, and proceedings threatened, the company promptly absorbed the opposing interests, while since then they have acquired many other patents and smaller manufacturing concerns, and have put others out of competition by actions for infringement. Although by this characteristically American policy the company practically monopolised the accumulator business for some time, and still control the making of the ordinary types of pasted plates, yet it is without doubt largely due to them that within a period of less than 10 years the American engineers have been brought to appreciate the advantages and possibilities of the storage battery and that they now make use of it as freely as on this side.

Just as was the case with the chloride cell in this country, their earlier types contained positive electrodes, produced by reversing chloride negatives; and they, too, abandoned this for a formed plate substantially the same as the "R" type of the Chloride Electrical Storage Company, but which they term the "Manchester" type. As the processes involved in the manufacture of both positives and negatives have already been described on page 407 *et seq.* they need not be further dealt with here.

A number of different standard sizes of electrodes are made, ranging from the "B" type, only 3in. by 3in., to the "H" type, 15½in. by 30¼in. They are all so designed that each gives twice the output of the size next below it. The actual figures of output per positive plate are given below; also the charging rates and size of plate. The electrodes are mounted in the cell either on the edges of the box itself or on glass slabs.

Type of Cell.	Dimensions of Electrodes.	Output at Rate of Discharge in Hours.				Normal Charging Rate.
		1	3	5	8	
B	3×3	...	3½	4½	5	5
C	4½×4	...	7½	8½	10	1½
D	6×6	...	15	17½	20	2½
E	7½×7½	20	30	35	40	5
F	11×10½	40	60	70	80	10
G	15½×15½	80	120	140	160	20
H	15½×30¼	160	240	280	320	40

PRESENT-DAY CELLS

In addition to the above types of electrodes a number of others are made up in ebonite boxes specially for use in electrically-propelled vehicles. Also, for this purpose, a new type has recently been brought out, termed the "Exide" accumulator, which contains pasted electrodes and gives an output of 4.5 ampere-hours per pound of complete cell. The positive electrodes are $\frac{7}{32}$ in. thick and their supports a kind of grid consisting of vertical bars connected by horizontal surface bars of triangular cross-section with their bases outwards and staggered relatively to those on the other face of the plate. By this construction the active material when pasted into the supports takes the form of thin continuous strips running from top to bottom and with the horizontal surface bars embedded in them. The negative electrodes are of the central conductor type, the support being a sheet of perforated antimonious lead with a frame cast round it. The perforations are not cut but pushed out so that the metal sticking up affords a better hold for the active material. The electrodes are separated by vertically ribbed diaphragms of wood and, pressing against the faces of the positives, flat sheets of perforated ebonite. The electrolyte has a maximum density of 1.300.

"Gould" Accumulator.

The cells of the Gould Storage Battery Co., of New York, contain formed electrodes only. The supports are prepared by a simple process which enables an extremely large exposed surface to be obtained relatively to the weight and area of the



FIG. 223.—Section through "Gould" Plate.

plate. Sheets of pure rolled lead are passed to and fro between two rotating spindles, each carrying a series of steel discs spaced a small distance apart by washers of a suitable thickness. The lead is not actually cut by the discs, but, is spun or drawn up into the spaces between them, and so a ribbed and grooved support is gradually produced. The spinning is continued until the plate is nearly penetrated through and only a thin core remains at the centre. All except the smallest sizes of electrodes are spun in sections or

panels, between which strengthening bars of solid metal of the thickness of the original sheet are left. Fig. 223 is a section through a plate two panels wide. The shaded portions show the surrounding frame and the dividing bar in cross-section; the unshaded portion, one of the ribs in profile. Figs. 224 and 225 illustrate a positive and negative respectively of the "S" type, $15\frac{1}{2}$ in. by $15\frac{1}{2}$ in.

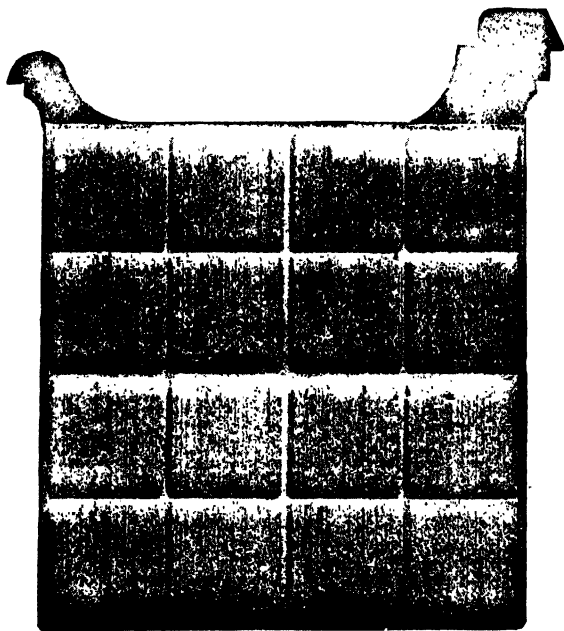


FIG. 224.—"Gould" Positive.

By this method of construction the lead may be subdivided to almost any extent, and yet every portion of it will possess the utmost density and a homogeneous structure which enables it to offer the best possible resistance to the disintegrating effects of local action. The actual thickness of the ribs and grooves is determined by the class of work for which the electrodes are intended. For automobile cells which will give 4,000 to 6,000 miles of service before repairs are necessary the ribs are made less than $\frac{1}{100}$ in. thick. For stationary cells the ribs are about $\frac{1}{40}$ in. thick, and the supports have an

actual surface nearly twenty times that of one of their sides, or about 200 sq. in. per pound of plate. For train lighting cells, which have to withstand much rough usage, still thicker

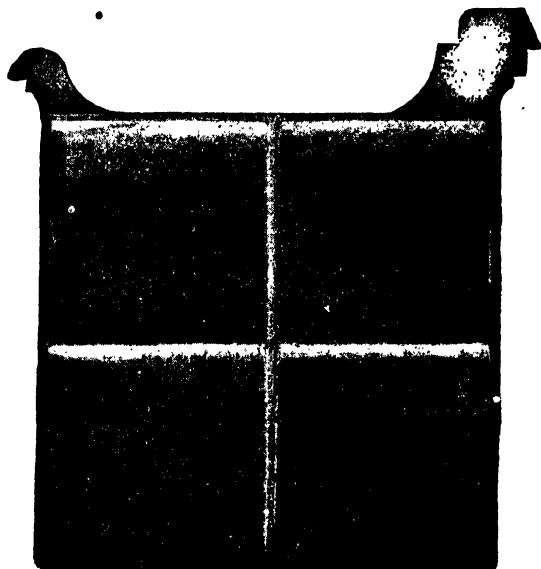


FIG. 225.—“Gould” Negative.

ribs are employed. Some particulars per positive plate of the various standard types of cell supplied by the company are given below :—

Type of Cell.	Dimensions of Electrode.	Output at Rate of Discharge in Amperes.			Normal Charging Rate.
		3	5	8	
K	3 × 3	3·7	4·4	5	0·75
L	4 × 4	7·5	8·7	10	1·5
M	6 × 6	15	17·5	20	3
N	7½ × 7½	30	35	40	5
O	10½ × 10½	60	70	80	10
S	15½ × 15½	120	140	160	20
T	15½ × 31	240	280	320	40
Train lighting	7½ × 9	...	33	37·5	7·5
E V automobile	{ 5½ × 7½	27	9
	{ 5½ × 9	30	9

"Willard" Accumulator.

These cells, manufactured by the Willard Storage Battery Co., of Cleveland, contain formed positives and negatives of the ribbed type. The plates are made by cutting thin leaves or ribs from the surfaces of a sheet of pure rolled lead, and setting them up to an angle of about 20deg. with the horizontal, thus forming a series of upwardly-inclined shelves. In the positive support every fourth rib is about twice the thickness of those intervening. The actual surface of the supports is about 16 times their nominal area. It is claimed that the additional peroxide produced by local action during

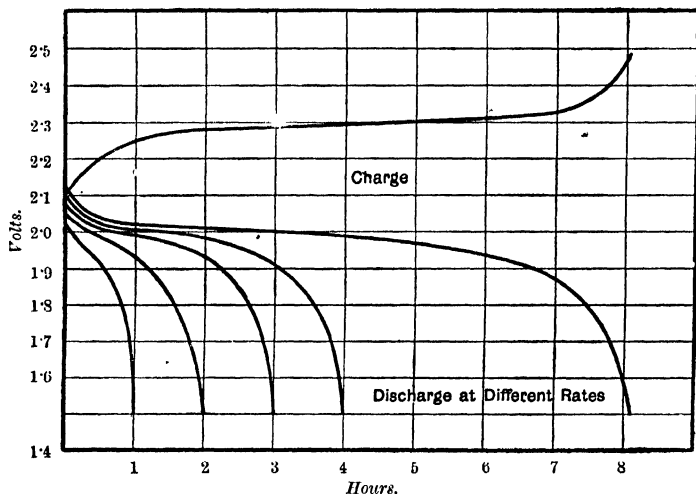


FIG. 226.—Discharge Curves of "Willard" Cell.

the life of the cell finds room for itself by pushing the leaves a little further apart, and causing them to assume a more nearly horizontal position—the plate, in fact, becomes somewhat thicker. Fig. 226 gives the curves of P.D. of a "Willard" cell when discharging at different rates, and when re-charging.

Besides the cells intended for stationary work, two types are also made for use in electrically propelled vehicles. In these cells the plates are separated by ribbed and perforated sheaths of ebonite, which surround the positives.

In certain small-sized cells of low output, two electrodes only are employed. Their shape is cylindrical, one standing within the other, and their adjacent surfaces are ringed with almost horizontal ribs cut in a continuous spiral. This is called the "Concentric" accumulator.

"American" Accumulator.

The American Battery Co., of Chicago, used to make a type of strip electrode called the "Morrison-Planté" (see pages 97 and 98), but they now employ formed and grooved positives and negatives in all their cells. The grooves are cut in a plate of pure rolled lead at right angles to its surfaces; but it is then passed between rollers, which bend up the ribs until their outer edges rest one on another. Upon formation, the peroxide gradually pushes the ribs apart again, in proportion to the amount of additional space it requires. Besides the horizontal grooves, two or three vertical ones are also cut at intervals on each side of the plate, dividing up the ribs into smaller sections and providing spaces into which they can extend when growing in the direction of their own length.

"Porter" Accumulator.

The cells of the Porter Battery Co., of Chicago, are fitted with Faure type electrodes. Two kinds of supports are described in the specifications. One consists of a series of horizontal undercut bars joined together by an upright at either end. The cross-section of the horizontal bars tapers rapidly from the surfaces towards the centre of the plates, and the active material between them takes the form of long horizontal six-sided prisms, two of whose faces are exposed to the electrolyte. The uprights are pierced with hexagonal holes of the same size, so as to give direct access of the liquid to the end of the prisms also. The other support has two series of thin flat horizontal bars set on either surface of the plate, and connected by vertical strengthening bars which pass below and between them.

Electrodes, mounted in the usual way in lead-lined or glass boxes, are supplied for stationary use; but a speciality is made of light-weight cells for electric automobiles. These

yield an output on a five-hour discharge rate of about six ampere-hours per pound of complete cell. Fig. 227 gives the curve of discharge P.D. at about a three-hour rate of one of these cells.

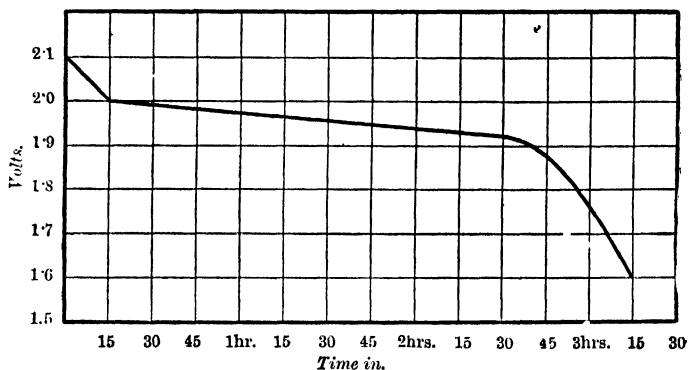


FIG. 227.—Discharge Curve of "Porter" Cell.

"Clare" Accumulator.

The International Storage Battery Co., of Boston, manufacture this type of cell, some of the earlier forms of which, such as that illustrated on page 53, were known as the

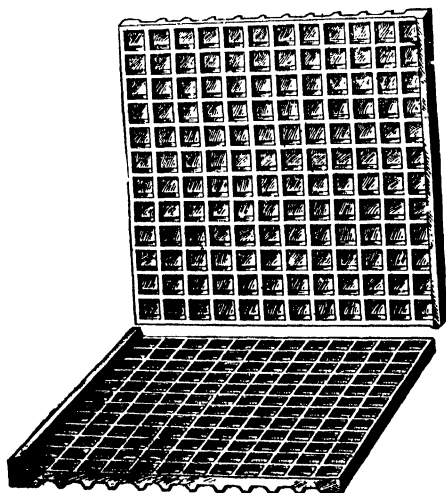


FIG. 228.—Inside View of Porous Supports for Active Material of "Clare" Electrode.

"Hatch" accumulator. The raw active material is packed into the cellular surfaces of two plates of porous earthenware similar to those shown in Fig. 228. They are then placed together with their pasted faces inwards, and their sides are united by an acid-proof cement. The ribs at these edges are somewhat deeper than the network of ribs by which the cellular spaces are bounded and flush with which the active material has been finished off, so a narrow opening remains between the plates, as may be seen in Fig. 229, and into this

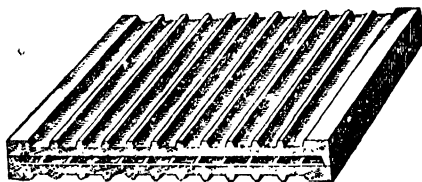


FIG. 229.—Outside View of Porous Supports of "Clare" Electrode.

a sheet of lead, about $\frac{1}{32}$ in. thick, is inserted, to form the conductor to the active material on either side of it. The complete electrodes are mounted with the ribs on the outside of the earthenware plates in a vertical position, and in direct contact in adjacent plates, so as to provide upright channels in which the electrolyte can circulate.

"Reuterdaahl" Accumulator.

The makers of these cells are the Reuterdaahl Electric Co., of Providence. Here again, as with the type of cell just described, the actual support for the active material is almost wholly provided by a non-conducting structure. This consists of a frame of ebonite or specially prepared wood, closed in by two sheets of perforated ebonite bolted to it. The ends of the bolts projecting on either side also serve as spacing pieces between adjacent electrodes. According to the patent specification the conductor is made up of a number of rods of lead, of circular or other cross-section, depending from a horizontal bar to which they are all united, generally being cast in one piece with it. The bar rests on the top of the frame, while the rods pass down into its interior through suitable openings

and have the active material compressed round them. Other forms of conductor appear also to be employed, but they are in all cases of antimonious lead cast under pressure.

The automobile cell of this make weighs 22lb., and gives an output of 4.5 ampere-hours per pound at a three-hour rate.

"Sperry" Accumulator.

The National Battery Co., of Buffalo, are the manufacturers of cells embodying various features described in Sperry's patents and more especially designed for autocar work. The active material of all the electrodes is prepared from a mixture of electrolytic or spongy lead, with 15 to 20 per cent. of litharge, a small quantity of alkaline sulphates, and a solution of ammonia or caustic alkali. This material is applied to supports of thin sheet lead, horizontally corrugated,

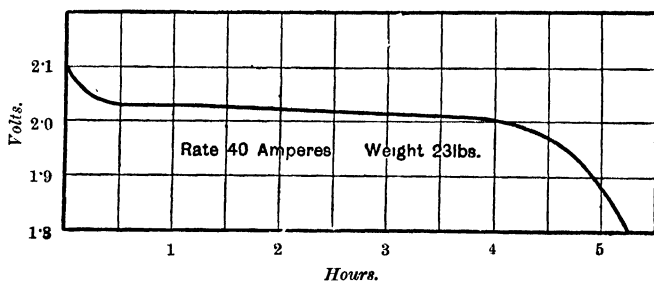


FIG. 230.—Discharge Curve of "Sperry" Cell.

and perforated in such a way as to turn back small triangular flaps of metal which stand out at right angles on either side. The electrodes are then subjected to great pressure, which welds the active material into a coherent mass and, forcing it through the perforations, securely binds it to the support. At the same time the projecting flaps are burned over and so further ensure the maintenance of a thorough contact between the two.

The electrodes are mounted in the cells wrapped in porous protective sheets consisting of an openwork cotton fabric converted into pyroxylin by suitable treatment, and covered on both sides by a layer of "sulphite fibre," i.e., pure cellulose, applied under pressure. These envelopes are ribbed vertically,

and the separators of thin perforated ebonite introduced between the electrodes are also corrugated.

To moderate as much as possible the mechanical shocks to which the plates are necessarily subjected in road traction, the ribs upon which they rest at the bottom of the containing box are tipped with rubber but slightly vulcanised, and this, being somewhat yielding, forms a sort of elastic cushion.

Fig. 230 gives the discharge P.D. curve of a Sperry cell weighing 23lb. complete, and discharging at 40 amperes—about a five-hour rate. Under these conditions it gives an output as high as 9 ampere-hours per pound of cell.

“Osburn” Accumulator.

These cells are specially intended for automobile work and a somewhat ingenious method is adopted for preparing a much lighter form of grid support than can be obtained by

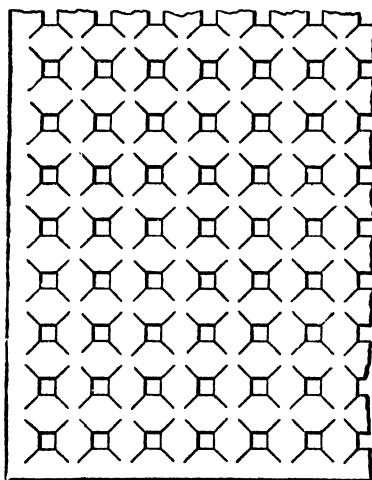


FIG. 231.—First Stage of “Osburn” Grid.

casting. Thin sheets of lead are passed through a perforating machine which punches out square holes with cuts extending diagonally from each of their corners, as shown in Fig. 231.

The nearly severed sections of metal that remain are then turned over at right angles to form the side walls of a grid,

illustrated in perspective in Fig. 232^a and in plan, partly pasted, in Fig. 233.

The separators between the plates are thin sheets of ebonite with horizontal slits through which vertical ebonite rods are woven in and out.

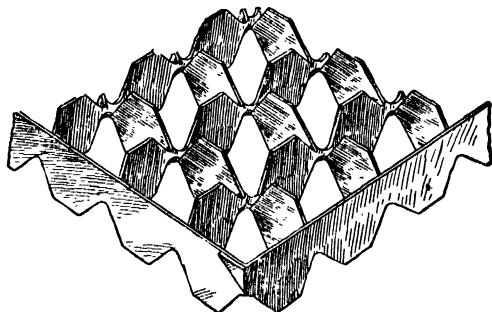


FIG. 232.—"Osburn" Grid

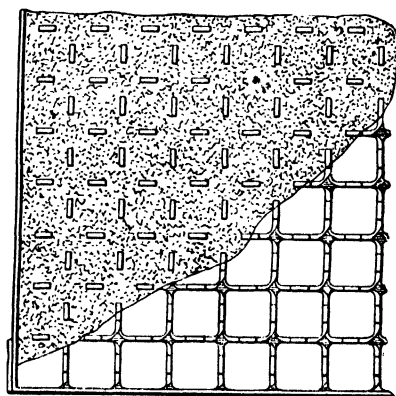


FIG. 233.—"Osburn" Electrode.

"Conrad" Accumulator.

The electrodes in these cells are of the pasted type, with supports consisting of horizontal triangular section bars whose bases alternately face in opposite directions. The cells have been employed in autocars by the Hewitt-Lindstrom Co., of Chicago.

CONTINENTAL CELLS.

"Tudor" and "A. F. A." Accumulators.

The manufacture of accumulators in accordance with M. H. Tudor's methods and patents was originally commenced in Belgium in the early eighties. In 1887 a factory was established at Hagen in Westphalia, and this concern, afterwards evolved into the Accumulatoren-Fabrik Aktien-Gesellschaft, has since been the one most largely interested in the technical and commercial development of Tudor's grooved electrodes, but they are now also made in England and several other countries of Europe.

The first positive plates were a sort of combination of the Faure and Planté systems. Having been formed up to about one-quarter or one-third of their ultimate output by electrolytically attacking the support itself, their grooves were then filled with the usual paste of red-lead and sulphuric acid, which, after peroxidisation, supplied the remainder. This pasted active material was only expected to remain in position for a year or so, and when it fell away, the additional peroxide produced by local action during this period, was sufficient to take up its work. The use of applied active material has now been abandoned for some years and the entire output is provided from the outset by Planté-formed peroxide. The present types of both positive and negative plates are closely similar, except for difference of sizes, to those of the Tudor Accumulator Co., already described on page 410, *et seq.*, so they need not be further dealt with here. Some early forms of Tudor electrodes are shown on pages 85 and 86.

"Hagen" or "K. A. W." Accumulator.

The electrodes of the Kölner Accumulatoren-Werke Gottfried Hagen, are of the pasted type with double-lattice grid supports. Some of the earlier forms of grid have already been illustrated in Figs. 22 to 24. The modern design consists of two horizontal series of triangular bars facing each other on either side of the plate and connected at intervals by vertical rectangular bars which extend the whole thickness of the electrode from surface to surface. The triangular bars have their apices pointing inwards and are less than half the

thickness of the electrode, so spaces are left at the middle of the plate between each pair of bars into which the active material penetrates from adjacent sections and unites them into a continuous whole. The result may be likened to the right-hand grid in Fig. 23, but with each vertical row of studs joined up so as to form a solid wall of metal.

Besides the various sizes and designs of cells for ordinary stationary purposes, an automobile type is also made with electrodes only 3mm. or about $\frac{1}{8}$ in. thick, which gives an output of about $4\frac{1}{2}$ ampere-hours per pound of complete cell at a five-hour discharge rate.

"Pollak" Accumulator.

The electrodes manufactured by the Accumulatoren Werke System Pollak, of Frankfort-on-Main, embody several somewhat unusual features of design and construction. Sheets

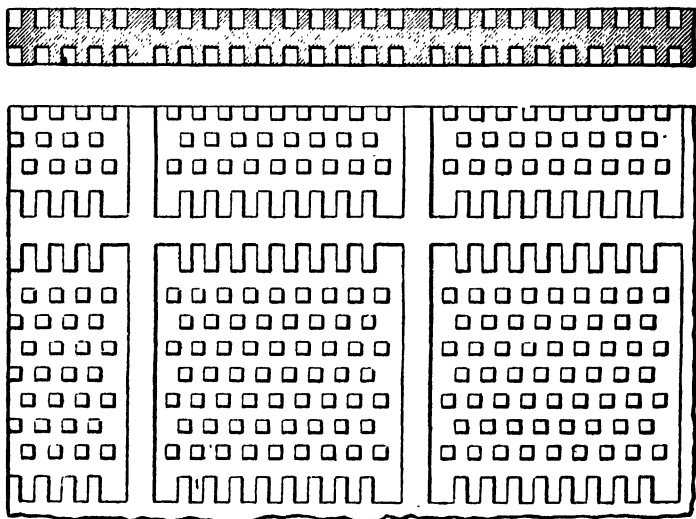


FIG. 234.

of pure lead are passed between massive steel rollers, fitted on the outside with steel rings, which have teeth cut upon them suitable to the pattern it is required to impress on the lead. By this means the sheets are covered on both sides

with rectangular recesses, in which are left standing a large number of projections or pins, as shown in Fig. 234. The sheets are then cut up into plates of any desired size, and lugs burned on to them for the purposes of mounting in the cell and connecting up. The complete support is not pasted with lead oxides, but is filled with spongy lead obtained by the electrolytic reduction of lead carbonate in an alkaline

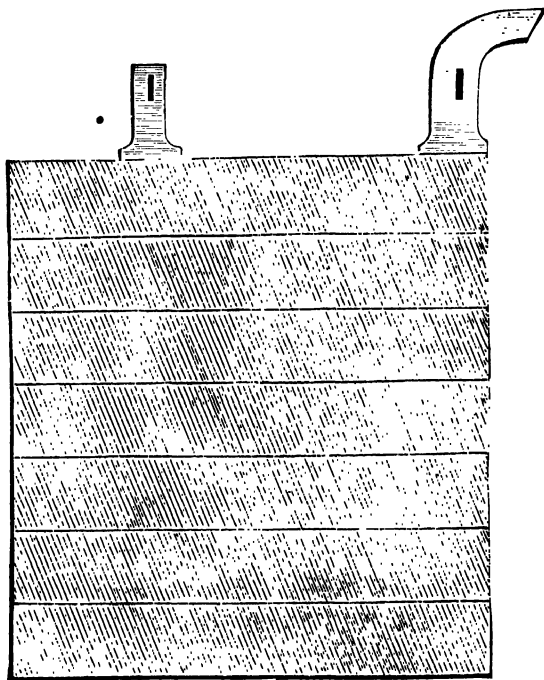


FIG. 235.—“Pollak” Large-surface Positive.

solution. This active material is consolidated and forced into thorough contact with the support by a process of compression, which at the same time burrs over the edges of the pins. The electrode is now ready for use as a negative, or for conversion into a positive by reversal.

The sheet lead from which the supports are constructed is rolled in two different designs. The one illustrated in the figure is used for all negatives, and for positives in cells to be

discharged at slow rates, or where weight is a consideration. The other has a larger number of pins spaced more closely together, and is intended for positives which have to endure rapid discharges. Quite recently, however, a large surface Planté-type plate has been introduced for this purpose (see Fig. 235).

“Khotinsky” or “Bleistaub” Accumulator.

This type of cell is manufactured by the Electricitäts-Gesellschaft, of Gelnhausen. The name “Bleistaub,” or “lead dust,” is derived from the raw active material of the electrodes, which consists of lead mechanically reduced to dust by blowing steam through a pipe connected with a vessel of the metal in a molten state. The lead is sucked up

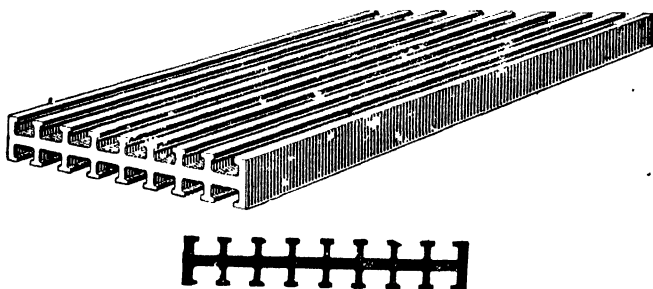


FIG. 236.—“Bleistaub” Support.

on the injector principle, and a jet of mingled steam and lead delivered into a suitable receptacle. Although the metal is by this means obtained in a state of extremely fine subdivision, it possesses none of the properties of electrolytically prepared spongy lead or true active material until it has been subjected to a formation process just as if it were a solid plate. The dust is intimately mixed with a considerable volume of powdered pumice-stone, worked into a stiff paste with water, and then packed into supports built up of grooved strips of lead about $\frac{1}{4}$ in. thick and $1\frac{3}{4}$ in. wide, and of the design shown in Fig. 236. The strip is produced by forcing lead under hydraulic pressure through suitable dies, and when cut up into a number of pieces

of the same length and burned into two vertical end bars it constitutes an electrode, as illustrated in Fig. 237. Owing to its large surface of contact with the electrolyte, the lead dust peroxidises rapidly on formation, and, as it does so, increases very considerably in bulk. This is why an admixture of pumice-stone is employed, for without some such provision the active material would burst its support. As it is, the strips expand somewhat, and their sideways growth is allowed for by spacing them a small distance

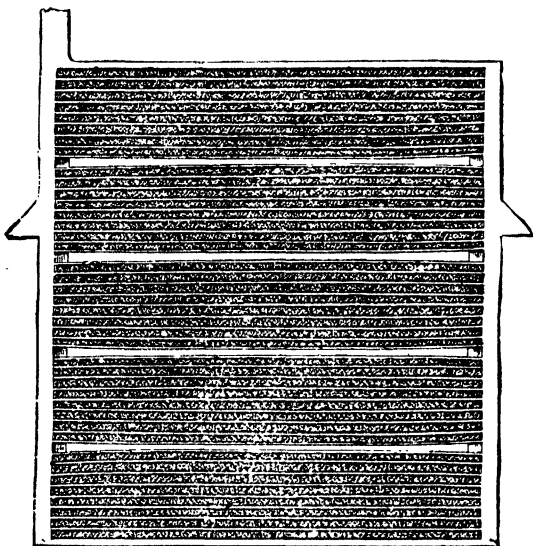


FIG. 237.—“Bleistaub” Electrode.

apart in the electrode. The bulge of the strips and the internal spaces can be observed in the figure, which represents a formed plate.

Cells containing electrodes of the same kind as those just described were made in France for some time under the title of the “Pulvis” accumulator.

“*Lehmann*” Accumulator.

The makers of these cells are the Berliner Accumulatoren- und Elektrizitäts - Gesellschaft. Their most distinctive feature is the ribbed type of positive with cross-grooves and a

zig-zag core which has been already described, and illustrated in Fig. 200. The negatives are of the pasted grid variety. Fig. 238 shows a form of cast grid support, designed by Dr. Lehmann, which used to be known as the "Mulden" accumulator. Fig. 239 gives the pasted plate. It is a sort of double-lattice support, having alternate strips of grid-work on either side, connected by bridge-pieces passing through its thickness.

Besides their cells for stationary and general use the Berliner Company also construct a number of types for portable purposes, in which nothing but Faure type electrodes

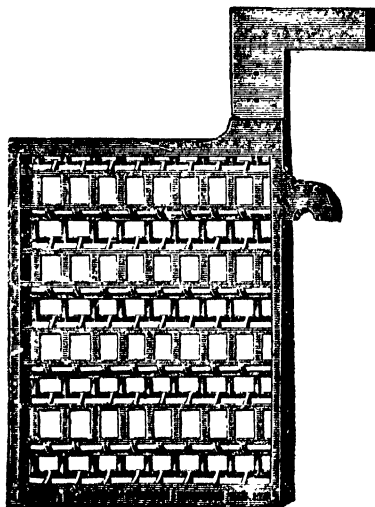


FIG. 238.—Lehmann's "Mulden" Electrode (Unpasted).

are employed. The oxides are mixed with various organic compounds in accordance with Hammacher's patents. The supports are simply grooved or undercut rectangular frames of hard lead, divided either into two panels by a cross-bar or four panels by two diagonal bars, and they are filled with a mass of active material. For autocar propulsion, a special type of cell is made with differently designed electrodes capable of withstanding high rates of discharge, but not

having so large an output for weight as the others. Its yield is about 5 ampere-hours per pound of complete cell at a 5-hour discharge rate.

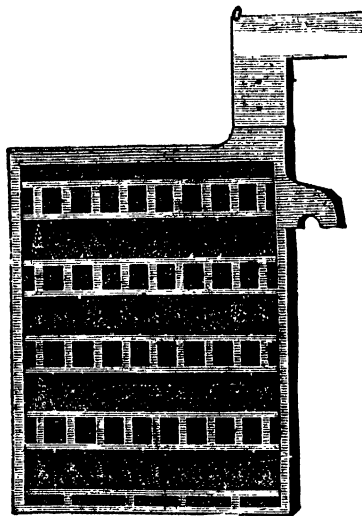


FIG. 239.—Lehmann's "Mulden" Electrode (Pasted).

"Boese" Accumulator.

All the cells manufactured by Messrs. W. A. Boese & Co., of Berlin, and known by their name, have, until recently, contained what in Germany are termed "Masseplatten." The English equivalent, "mass-electrodes," is only occasionally used in this country to signify plates containing large cakes or masses of active material and a minimum of support, and they are more frequently spoken of as being of the "Lithanode" type. The Lithanode and the Boese types of electrode are both alike, in so far as their speciality consists in a form of peroxide active material, which is claimed to combine porosity, strength and conductivity in an unusually high degree; but the methods of its preparation are in no wise similar. In the Boese plates the lead oxide is mixed with a solution in alcohol of coal tar residues or similar substances, and the mass is then filled into a rectangular hard lead frame of the size of the required electrode.

horizontal bar is separated from its neighbour by a small space which allows for the through circulation of the electrolyte,

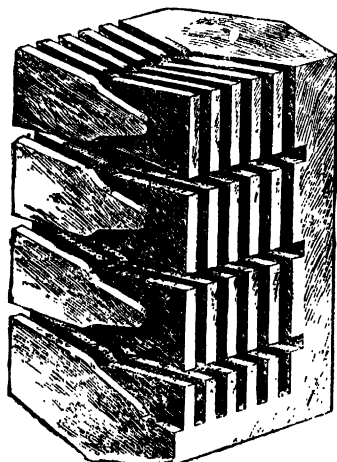


FIG. 241.—Detail of "Boese" Large-surface Electrode.

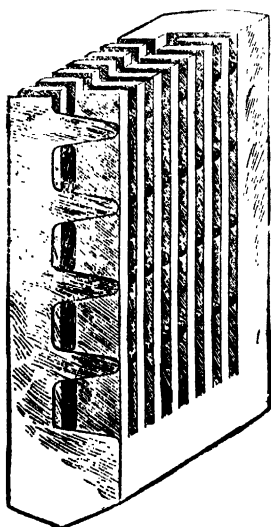


FIG. 242.—Detail of "Boese" Traction Electrode.

but they are all tied together and strengthened by stout vertical bars passing from top to bottom of the plate.

For traction cells a modified form of the above electrode is made. A small portion of this plate is illustrated in Fig. 242. It will be seen that the bases of all the triangular teeth directly above each other are here united to form two series of vertical bars, one on each side of the plate, while their apices are prolonged to reach right through to the opposite surface, and so increase the depth of the horizontal bars; but the internal spaces into which the electrolyte can penetrate still remain.

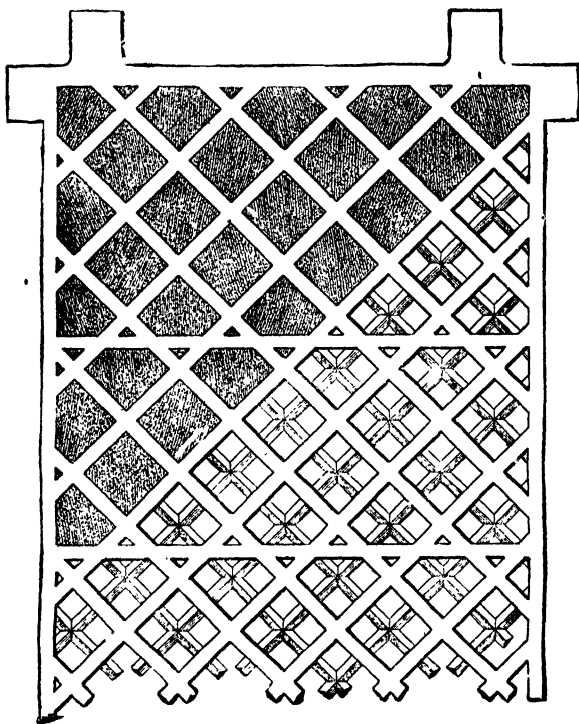


FIG. 243.—“Correns” Electrode.

With both these types of formed positives a pasted grid negative of hard lead is employed, and for traction cells of the lightest construction, or which only need to be discharged at moderate rates, all the electrodes are of the pasted kind. The supports are of the “Correns” double-lattice type, illustrated in Fig. 248. The two lattices are directly superimposed

on each other without any space between them. Their grid bars are of triangular section with the apex inwards, but the electrode is cast all in a piece.

"Behrend" Accumulator.

The stationary high discharge cells of the Behrend-Accumulatoren-Werke, of Frankfort-on-Main, contain pasted negatives and Planté-formed positives. The latter, which are of the "Wehrlin" type, are characterised by deep zig-zag grooves running from top to bottom of the plate, and so arranged that those on the one side cross those on the other. The actual surface of the support is increased from eight to ten times its nominal surface. The negative supports are cast grids with vertical bars cross-connected by slight triangular bars in such a way as to form strips of lattice work alternately on one side and the other.

In the stationary cells for low discharge rates only, all the electrodes are of the pasted type. In the smaller sizes of cells, for various portable uses, masses of active material, compressed and perforated and held in a frame of hard lead, are employed.

"Schulz" Accumulator.

The positive electrodes, manufactured by the Accumulatoren-Werke E. Schulz, of Witten-on-Rhur, are deeply grooved plates with a solid central core. The formation is effected by a rapid process, but not through the agency of acetic acid or other substances which might have a deleterious after effect. The negatives are of the pasted type, with grid supports.

"Watt" Accumulator.

The Watt Accumulatoren-Werke, of Zehdenick, chiefly use pasted electrodes of the Schäfer and Heinemann type. The supports consist of grids with horizontal bars of triangular cross-section, whose apices are turned alternately towards either face of the plate, and vertical connecting bars.

"Tribelhorn" Accumulator.

The Tribelhorn Accumulator Works, of Zurich, appears to be the only concern who construct storage batteries of the "series" or "high-tension" type. The electrodes are

circular, conical cast-lead trays or receptacles, covered inside and out with concentric grooves, which contain the pasted active material. They are piled one upon another, but insulated and spaced apart by glass balls, which rest in niches provided for that purpose, and the electrolyte is filled in between them. In this way each electrode is negative on one side, positive on the other, and, at the same time, serves as its own containing vessel. Apart from the details of construction which have been found necessary to render this arrangement at all practical, it is fundamentally the same as Philippart's early form illustrated on page 112.

Amongst other German accumulator makers are Dr. Pflüger & Co., of Oberschöne-weide; Moll and Palmer, of Freyburg; and Zinnemann & Co., of Berlin. The speciality of the two latter firms is cells of small and moderate sizes with pasted electrodes mounted for use as portable batteries or for autocar work.

French "Chloride" or "T.E.M." Accumulator.

La Société pour le Travail Électrique des Metaux, of Paris, was formed in 1889 to acquire Laurent-Cély's patents relating to the preparation of active material from lead chloride, and the method of its use in electrodes (*see* page 45). Although the commercial development of the chloride cell proceeded almost simultaneously in France and the U.S.A., the two companies in their early days worked independently of each other and by different methods, and it was not until later that they became in any way allied. Their after experiences were in several respects similar. The French company were also threatened with litigation by the owners of the older patents—Faure, Sellon and Volckmar—covering the use of applied active material and of grid supports; and they also bought out and absorbed their rivals and became one of the largest battery manufacturers in the country. They, too, found—and here the experience of the English makers coincided—that the new active material did not effect quite the revolution it was expected to do, and that its *employment had to be restricted chiefly to negative electrodes*: indeed, for certain purposes, the French company have even replaced these by pasted plates. They construct a variety

of types of positives, using one or another as may best suit the work to which the cells are going to be put. The following are the chief of them :—

A horizontally-grooved plate with central core and upwardly-inclined ribs. This is cast under pressure in antimonious lead, and is intended for pasting, and for repasting when its output falls too low. The ratio of the weight of active material to the total weight of the electrode varies between 15 and 22 per cent.

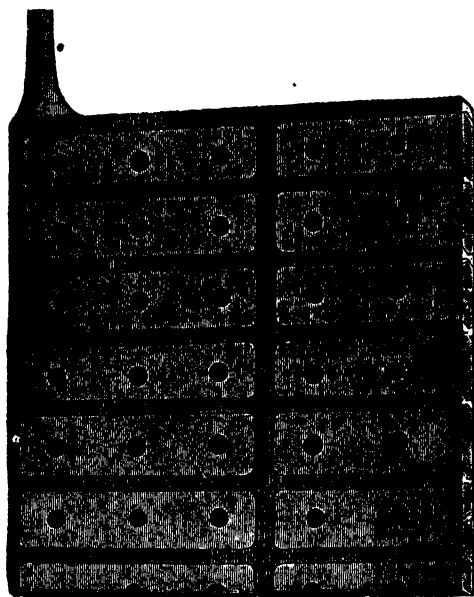


FIG. 244.—French "Chloride" Electrode.

A grooved plate with upwardly-inclined ribs but no central core. This is cast in pure soft lead, with the intention that, by the time the pasted active material has fallen away, its surface may become sufficiently formed by local action to take up the work. This electrode contains about 28 per cent. by weight of active material.

A plate constructed by casting a frame of antimonious lead round pastilles of lead chloride and then reducing them with

zinc in the manner already described on page 407. The active material represents 27 to 50 per cent. of the total weight of this class of electrode, according to its thickness. Fig. 244 shows a portion of one of these electrodes of the

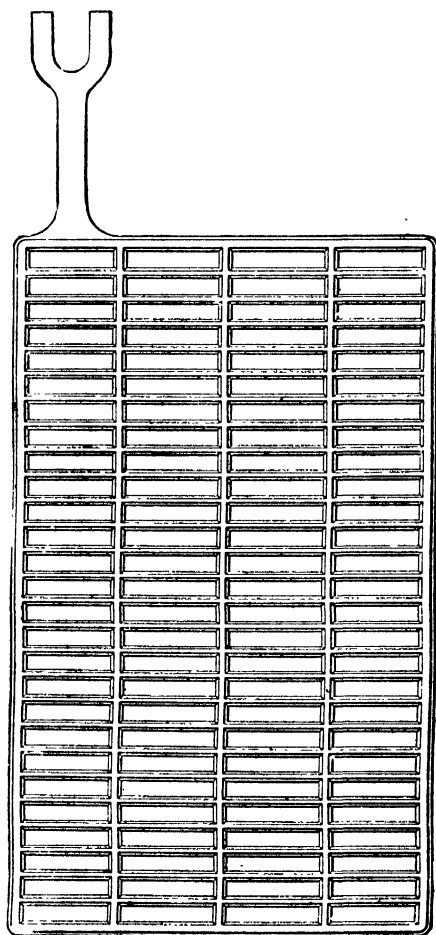


FIG. 245.—“T. E. M.” Pasted Electrode.

design used for the positives and negatives of the light-weight automobile cell. The positives are obtained by reversing the reduced lead plates.

A plate intended for extra light-weight automobile cells and consisting of a very slight pasted grid, such as is shown in Fig. 245. In this electrode the active material attains to 64 per cent., or two-thirds of the total weight of the electrode.

A Planté-formed plate, built up of strips of corrugated lead tape arranged horizontally and burned into two side bars, one of which is the main conductor. All the strips are slightly thickened in two places in order to keep them spaced a little

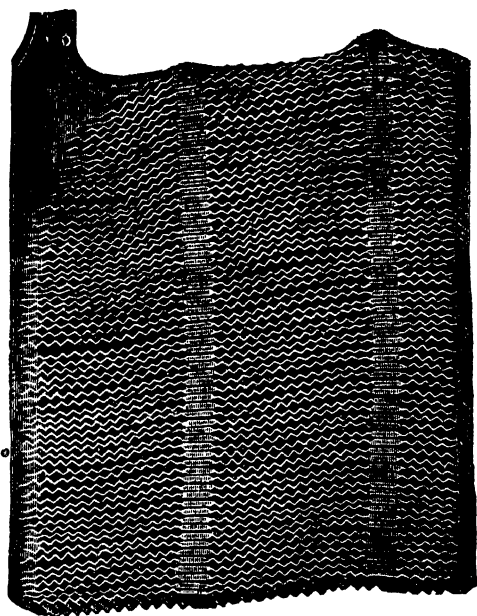


FIG. 246.—“T.E.M.” Strip Electrode.

apart, and they are also perforated at these points to allow the insertion of two light lead rods, which are burned to the top and bottom strips, but upon which the others work loosely up and down (see the portion of a plate shown in Fig. 246). This type of electrode constitutes the positive of the ordinary traction cell and is combined with a negative similar to that used in the light traction type and illustrated in Fig. 244.

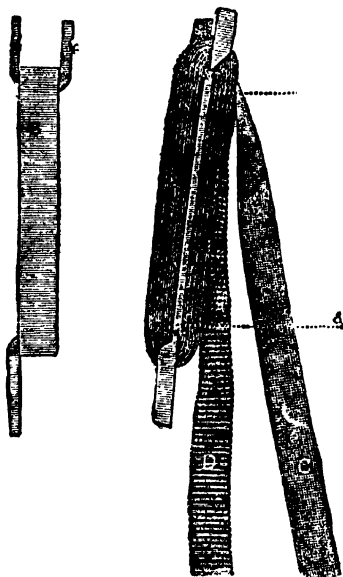


FIG. 247.—Construction of "Blot" Electrode.

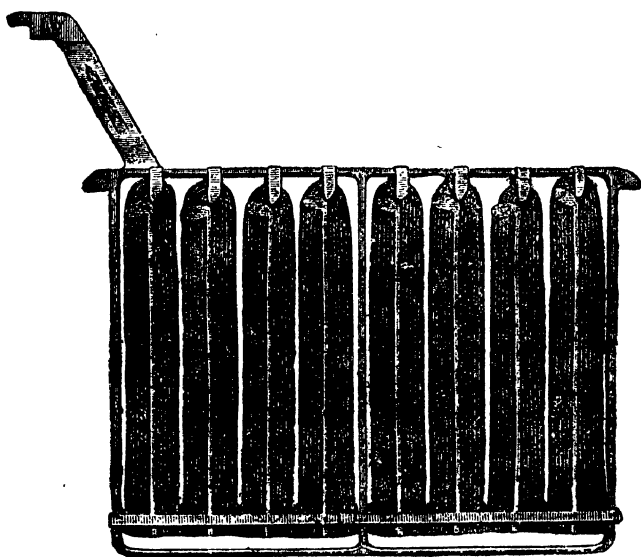


FIG. 248.—"Blot" Electrode.

"Blot" Accumulator.

The earliest design of the Blot electrodes has already been described and illustrated at page 98 and in Fig. 106. The method of constructing the modification afterwards adopted in practice may be briefly recapitulated here. Two lengths of pure lead tape or ribbon—the one embossed and corrugated, the other embossed only—are placed alongside and wound on a long core or shuttle of antimonious lead (*see* Fig. 247). The layers of tape having been burned together and to the core at both ends, the shuttle and its windings are all divided by a central cut at right angles to their length. A number of these half-shuttles, arranged with their cut ends downwards and burned into a suitable frame of hard lead constitute an electrode, as shown in Fig. 248. A band of metal round its lower part and burned to the cores prevents the ribbons from becoming displaced sideways. The finished plates are subjected to a Planté formation.

"Blot-Fulmen" Accumulator.

In cells intended for stationary batteries and general use the positives and negatives are all of the Blot type, but in

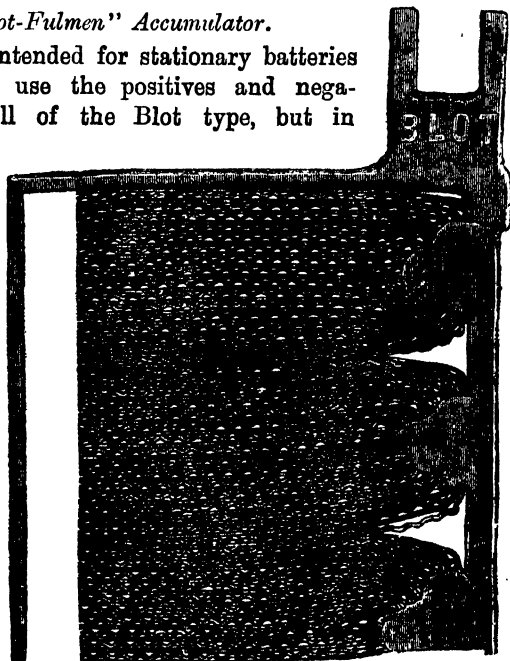


FIG. 249.—"Blot" Automobile Positive.

light traction batteries for automobiles and similar purposes pasted electrodes of the "Fulmen" type are employed. In these cells the layers of ribbon in the positives are placed horizontally instead of vertically, and the central cores are dispensed with. A part of a plate of this kind is shown in Fig. 249.

"D'Arsonval-Vaugeois" Accumulator.

In 1901, the Compagnie des Accumulateurs Électriques "Blot" introduced a new type of electrode, devised by MM. d'Arsonval and Vaugeois, which they claim to be much more

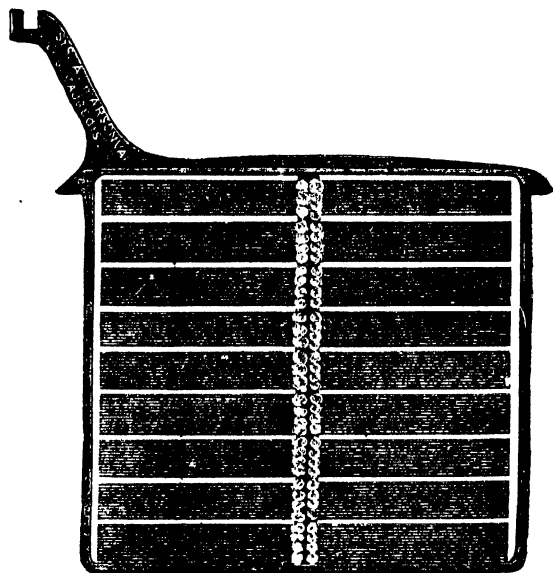


FIG. 250.—"D'Arsonval-Vaugeois" Electrode.

durable than the ribbon plates just described. The alteration consists in replacing the shuttles and their windings by grooved strips of lead obtained by forcing the metal through suitable dies under great pressure. Fig. 250 shows their plate for stationary cells, and Fig. 251 gives a view of one of the component strips. These are arranged horizontally, and

sufficient space is left between them and between their ends and the surrounding frame to allow for their growth in all directions. The electrodes are so designed that their weights, dimensions, outputs, methods of mounting, &c., are the same as those of the corresponding sizes of the Blot type. Fig. 252

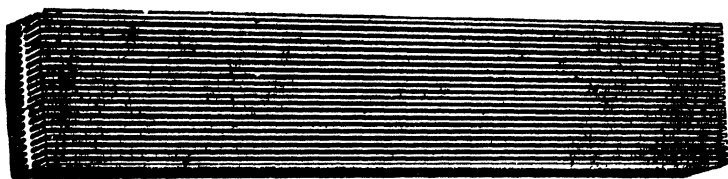


FIG. 251.—Detail of "D'Arsonval-Vaugeois" Electrode.

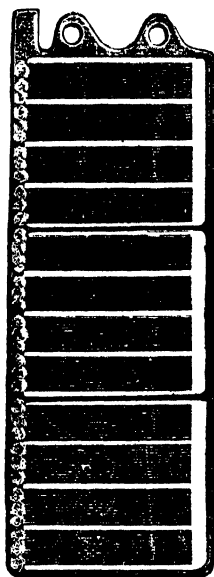


FIG. 252.—"D'Arsonval-Vaugeois" Traction Electrode.

illustrates the design of the traction plate used both for positives and negatives in the cells which run the tramcars on the St. Denis-Madeleine and the St. Denis-Opéra lines in Paris.

"Fulmen" Accumulator.

La Société Nouvelle de l'Accumulateur Fulmen, of Clichy, has from the first made a speciality of light-weight cells for automobile purposes, and their manufactures have become widely known in this connection. Except in the Blot-Fulmen type just described, all their electrodes are of the pasted kind. A variety of designs have been tried during the last few years and Figs. 253 and 254 show two of the most recent, intended

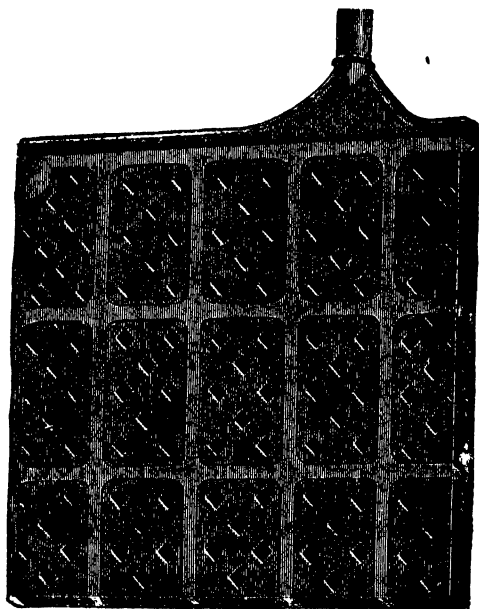


FIG. 253.—"Fulmen" Positive

for use as positives and negatives respectively. In both cases the support consists of two extremely thin hard lead grids riveted together after being pasted. In the negative, the grid-bars are further cross-connected by a network of slight surface bars which distribute the work more uniformly over the whole plate. The active materials are perforated at frequent intervals to give a freer access of electrolyte to their

interior. In another design of electrode the grid-bars run diagonally, and the apertures are diamond shaped instead of rectangular.

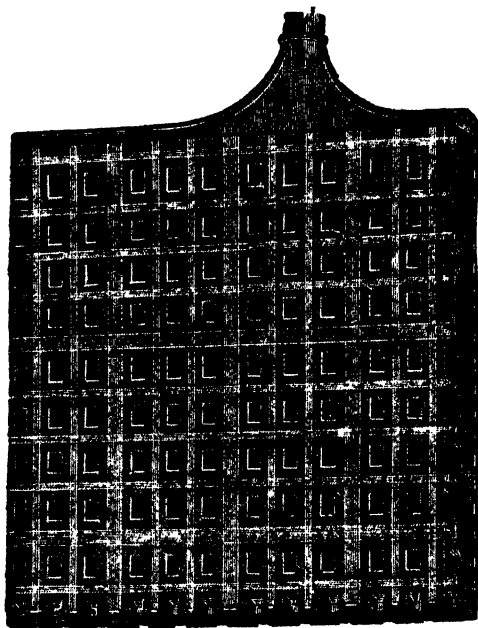


FIG. 254.—“Fulmen” Negative.

“B. G. S.” Accumulator.

The chief features of the Fulmen electrodes, namely, their two-part grids of antimonious lead and perforated active materials, are common to several other French makes of light autocar cells, and they occur in those of MM. Bouquet, Garcin and Schivre, with but slight differences in the details of design and the proportion of parts which do not necessitate further description.

“Heinz” Accumulator.

Two types of these cells are made by A. Heinz & Cie., of Levallois, the one for stationary use and the other for traction purposes. The same kind of negative electrode is

employed in both cases, and Fig. 256 shows the design of the support for the traction plate. It is cast in two separate pieces each of which is a gridwork of rectangular bars, 3mm. deep, further subdivided by a number of slight and closely spaced horizontal surface bars. These are of triangular section with the apex pointing inwards and are little more

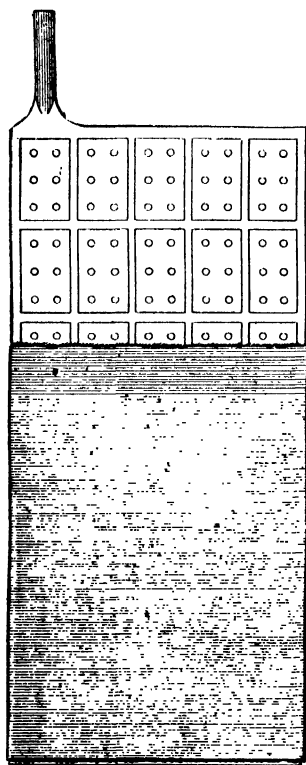


FIG. 255.—“Heinz” Positive.

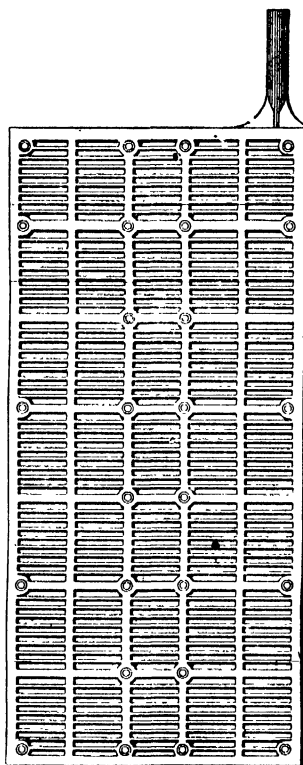


FIG. 256.—“Heinz” Negative.

than 1mm. deep, so when the grids are put together only the main bars come into direct contact and a clear space for active material is left between the others. The two halves are united by pins projecting from the one and engaging in corresponding holes in the other, to which they are firmly riveted and burned; but previously to this the raw active

material of litharge mixed with magnesium sulphate solution is pasted into each half separately.

The traction type positive that goes with the above negative is illustrated in Fig. 256. The support is merely a large celled grid of hard lead cast all in one piece. Its thickness is 4.8mm. and the apertures are 30mm. high by 20mm. wide. The raw active material is composed of litharge and minium in equal proportions, mixed to a paste with distilled water. It is forced into the grid under pressure and, at the same time, each pastille is perforated with six holes which facilitate the penetration of the electrolyte to its interior. Previous to formation each electrode is wound with a thread of vulcanised asbestos to help keep the active material from falling out. The traction positives and negatives both contain a quantity of active material equivalent to about two-thirds of the total weight of the complete electrode.

The stationary type of positive is a vertically grooved plate with a central web. It is cast in pure lead and is filled with a paste of minium after a preliminary treatment in hot acid to prepare its surface and improve the contact between them.

“Majert” or “Union” Accumulator.

These cells are manufactured in France by the Compagnie Française des Accumulateurs Électriques “Union” of Neuilly-sur-Marne. Their positive electrodes are horizontally ribbed plates with a central core, but without the usual surrounding frame of solid metal. The method of their preparation is unusual and interesting. A rectangular plate of rolled lead about 7mm. thick is affixed to the table of a kind of shaping machine which is traversed by a cutting tool, perpendicularly fixed and with a reciprocating motion. This ploughs obliquely into the lead and turns up a strip of metal at right angles to the plate, while after each stroke the table moves forward a short distance; and in this way a series of parallel ribs of any desired depth, thickness and spacing are produced. Fig. 257 shows the tool in operation, and Fig 258 a section through the plate, about three times enlarged. The supplementary arm carries a smaller roller which presses against the back of the tool to prevent it springing away from its work, and ensures a straight and uniform cut.

When one side of the plate is finished it is turned over and the other side cut similarly, a core of solid metal 1mm. to 2mm. in thickness being left at the centre.

It is possible with this machine to obtain as many as 35 ribs to the centimetre, and an electrode with an actual surface



FIG. 257.—Manufacture of "Union" Positive.

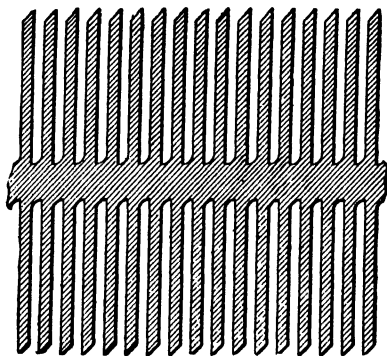


FIG. 258.—Enlarged Section of "Union" Positive.

35 times its nominal surface; but this enormous increase necessitates the ribs only being about the thickness of a sheet of paper, and in practice 10 ribs per centimetre is a more usual figure. Even then, the ratio of actual to nominal surface is greater than can be realised with a cast plate, and it is

claimed moreover that the metal is denser and more homogeneous, and therefore more durable.

As negative electrode, a cast grid of the pasted type is employed. The design of the support is shown in Fig. 259. It consists of a number of vertical bars, cross-connected by closely spaced diagonal ribs, some of which slope in one

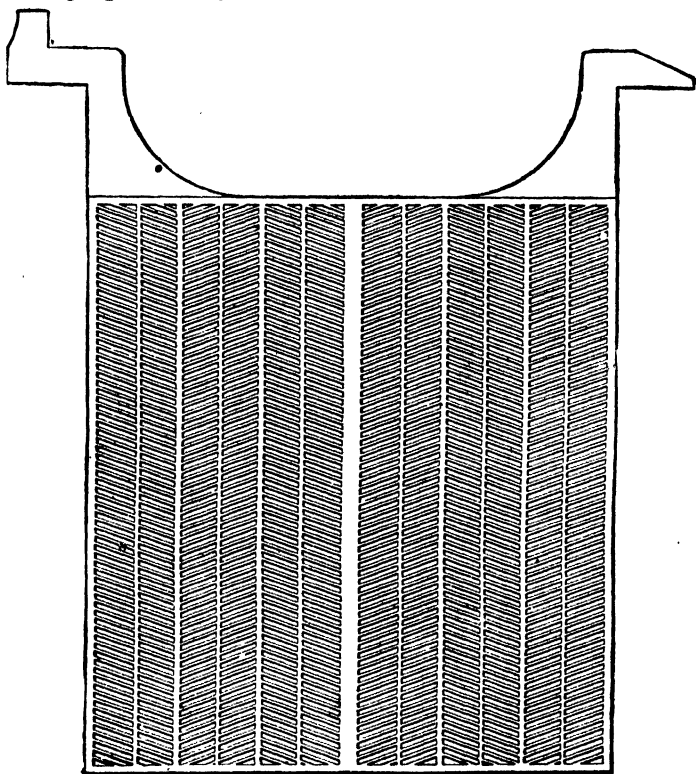


FIG. 259.—“Union” Negative.

direction and some in the other. The ribs are thickest at their centre and taper down to fine edges which project a little beyond the general level of the electrode. After pasting, these are burred over and set up so as to afford a better hold and support for the active material. Another form of grid is also made with the cross-ribs horizontal throughout.

"Phoenix" Accumulator.

The design of this cell is due to G. Philippart, and is somewhat peculiar. In the type first introduced, the electrodes were built up of a number of small rod-like elements about 3 in. long and $\frac{1}{4}$ in. in diameter. Fig. 260 shows the various stages of their construction. A rod of lead had two washers burned to it at the requisite distance apart, and a layer of pasted material then filled in between them.

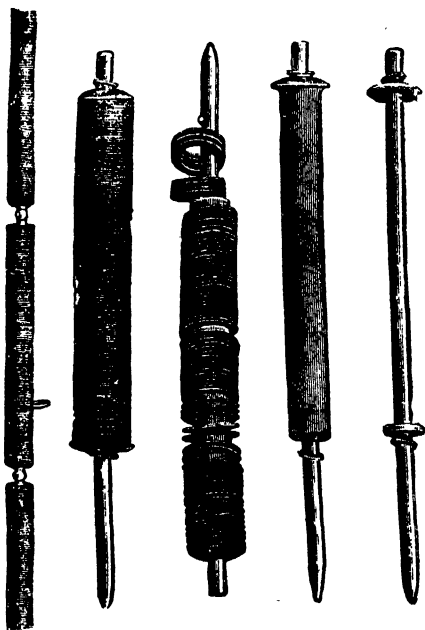


FIG. 260.—Details of "Phoenix" Electrode.

Upon this was threaded a number of washers of thin ebonite or the like, which were held in loose contact by two stouter end washers, this arrangement being claimed to provide good mechanical support for the active material, and yet at the same time allow a sufficient access of electrolyte to it.

Two or more of these rods were burned together end to end (in threes, as illustrated), and any number of the longer rods thus produced mounted in a cell (see Fig. 261), not with all the elements of the same polarity in a row, but so

arranged that each positive was surrounded by negatives on all four sides, and vice versa.

A later design of electrodes still preserved the cylindrical shape, but otherwise differed radically from the one just

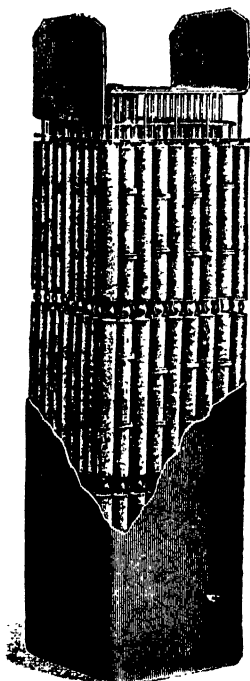


FIG. 261.—"Phenix" Cell.

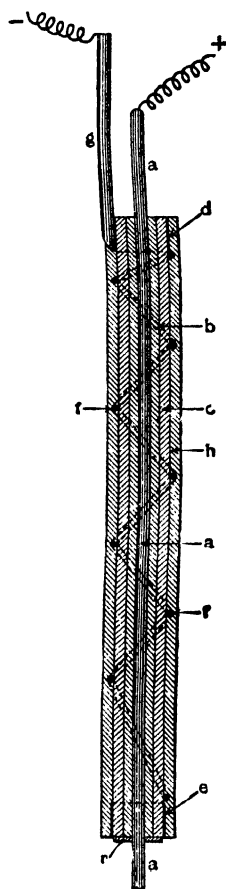


FIG. 262.—Later Type of
"Phenix" Electrode.

described, for each rod now consisted of a self-contained positive and negative, the former inside, and the latter concentrically around it. This arrangement is illustrated diagrammatically in Fig. 262. A rod, *a*, of hard lead is surrounded by a layer,

b, of peroxide active material, and then a tube, *c*, of porous earthenware. Upon either end of this are placed lead collars *d* and *e*, connected by a lead wire, *f*, wrapped spirally around the tube and covered by a layer of spongy lead, *h*. The whole cylinder is finally enclosed in a thin perforated sheath, either of lead or of some non-conducting material. The central rod is the positive conductor, and another rod, *g*, burned to the upper lead collar, is the negative.

The preceding type has in its turn been superseded by a later design brought out in 1902. In it the concentric arrangement is abandoned and a return made to separate cylindrical electrodes as in the first form, but differing considerably in the details of construction. Each positive consists of a porous pot, about $\frac{2}{3}$ in. in diameter and 9 in. long, containing a central lead conducting rod of coniform section, round which the red lead constituting the raw active material is placed. The negatives are lead rods, also of coniform shape, but so pasted with lead oxide as to bring them to a cylindrical form. Numerous small holes penetrate the surface of the active material, while it is supported and kept from touching the positives by a series of thin ebonite rings, in loose contact with one another, which are slid over each negative. In the cell electrodes of opposite polarity are disposed much as shown in Fig. 261, and one set of connections pass up through holes in the main terminal plate of the other set in a very similar fashion.

All these types of electrodes are especially intended for use where a large output for weight is necessary, and are capable of yielding about 6 ampere-hours per pound of complete cell at a five-hour discharge rate. The earliest type took part in the automobile accumulator competition of 1898.

"Max" Accumulator.

In a general way, this cell resembles the early type of Phenix accumulator. Its electrodes are also rods of lead, covered with a layer of active material and mounted in rows with alternate positives and negatives. Each rod is, however, insulated with a woven sheath of blue asbestos fibre, Fig. 263 is a perspective view of a number of rods connected up ready for use, one main conductor coming away from their

lower and the other from the top ends. In the latest construction the details of connecting up have been somewhat modified, and the ends of the rods are held top and bottom by zig-zag pieces, D, which are of lead and ebonite alternately. The pasting of the lead rod, cutting it off into lengths and covering with asbestos is all carried out by automatic machinery designed and patented by J. J. Heilmann.

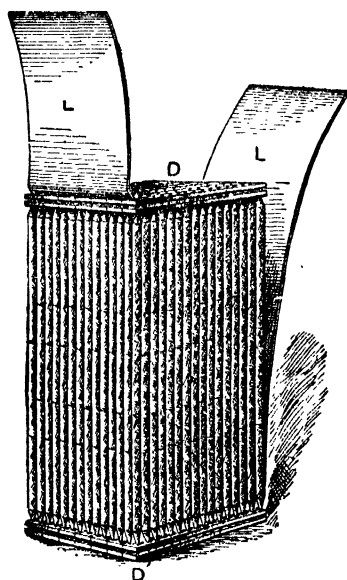


FIG. 263.—"Max" Section.

"Cheval-Lindeman" Accumulator

So far as the positive electrodes of this cell are concerned, they, like the two preceding ones, are of the rod type, with conductors buried in the active material, and an outer insulating support—in this instance, a perforated case; but the negative electrode is a distinctive feature. It consists of a single mass of spongy lead, filling in the body of the containing box right up to the side walls, but pierced from top to bottom with a number of cylindrical holes, lined with some perforated insulating material. The diameter of the

holes is such that they can each contain one of the rod positives and still leave an annular space for free electrolyte between the concentric sheaths. The current is conveyed to and from the negative active material by a number of vertical lead rods, which penetrate it between the apertures. The arrangement may be likened to a "Monobloc" cell, with a single common electrode of the pasted instead of the formed type, and negative instead of positive. It will be made quite clear by an inspection of Fig. 264, which gives a horizontal section through a cell. The small dotted circles are the positive conductors of perforated lead tube. The two larger dotted circles surrounding each of them are respectively the

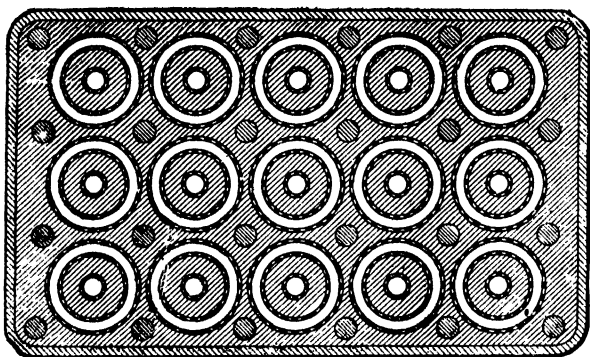


FIG. 264.—Section through "Cheval-Lindeman" Cell.

perforated outer walls of the positives and internal perforated linings of the negative. The small shaded circles are the negative conductors, and the other shaded portions are active material.

"De Dion-Bouton" Accumulator.

This cell contains pasted electrodes of the type illustrated in Fig. 265. The support is a double lattice grid, with oblong apertures. The bars on either side of the plate are not displaced relatively to one another, as is often done, but are directly facing. There is an internal space between the two lattices, but they are tied together by stouter vertical bars at frequent intervals,

Accumulators other than Lead/Lead Peroxide.

There is not much to be said here regarding such cells, because, although always a source of interest and hope to the inventor, very few of them pass into practical use, even for a

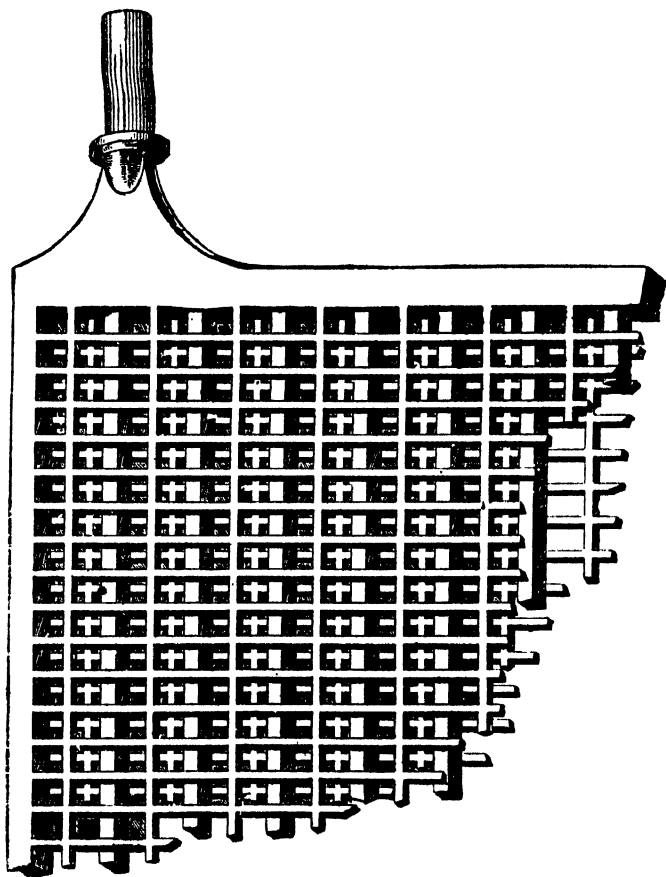


FIG. 265.—“De Dion-Bouton” Electrode.

limited period. Edison's new combination with active materials of iron and nickel oxide in an alkaline electrolyte has been the one most talked about, and all the particulars—chiefly obtained from patent specifications—available up to

the early part of 1901, have already been given in Chap. III., (see page 137, *et seq.*). Since then, nothing of much value has been published regarding it, nor has the Author been able to obtain any further information; and at the time of writing, November, 1902, its commercial application seems as far off as ever.

Apart from Edison's cell, most other recent attempts to vary the usual combination have been confined to the substitution of zinc or cadmium in place of the spongy lead at the negative, the metal being dissolved up by the electrolyte on discharging, and re-deposited again when charging.

The "Leecoll" accumulator was constructed on this principle. Its positive electrodes consisted of long tubes of porous earthenware, about 1 in. in external diameter, packed with active material. The tubes were closed with a plug, top and bottom, and a lead rod passing down their centre, served to collect the current and convey it to the external circuit. The negative support was an amalgamated copper wire gauze concentrically surrounding the porous tubes, but kept from contact with them by separators of thin glass rod. The positives were mounted in the cell in rows with spaces between them, and the gauze was so bent that the same sheet could surround all the tubes in a row. The negative active material was deposited upon the amalgamated wire from a solution chiefly composed of dilute sulphuric acid and zinc sulphate, but it was said to also contain cadmium sulphate and other salts. The Leecoll cells gave a large output for weight and were used for a time in electrically propelled vehicles with good results, but they are not now manufactured.

Zinc deposited upon copper wire gauze is also used as the negative electrode in New and Lucas' cell in conjunction with ordinary flat plate positives. The negative support is subjected to a special preliminary treatment to reduce the local action between itself and the zinc to a minimum. This cell has not as yet been put upon the market, but it is within the Author's knowledge that it has received some prolonged tests of a practical nature in connection with autocar work.

In the Commelin and Viau cell, cadmium is deposited from a solution of cadmium sulphate upon a support consisting of very thin sheet lead mounted on a celluloid backing and

covered with nearly horizontal ribs or shelves of celluloid to help keep the active material in position. Such details of construction as have been published do not suggest that the cell is of a very practical type. The negative may be employed in combination with a light form of positive built up of an ebonite grid packed with lead peroxide and riveted to a lead backing; or with hollow carbon electrodes supplied with oxygen under pressure and constituting a kind of gas battery.

This concludes the account of modern cells. So far as those intended for stationary purposes and batteries of large output are concerned it is not likely that any of importance have been omitted, but many of the new makes of light weight cells which are constantly being brought out for automobile propulsion have such a brief and butterfly-like existence that it is difficult to be certain if count has been taken of all of them.

Even during the compilation of this chapter some here described have finished their career, and doubtless others are now being hatched in the laboratory, or emerging through the patent specification into the light of publicity and practical usage.

INDEX.

(EXCLUSIVE OF NAMES OF CELLS AND ELECTRODES.)

(See List of CELLS AND ELECTRODES, p. 489.)

- Active Material**, Appearance of, 346
 - Coefficient of Support Contact of, 262, 267
 - Definition of, 9
 - Discharged, Composition of, 226
 - Expansion of, 255, 257
 - Output per Unit Volume of, 269
 - Output per Unit Weight of, 268
 - Pasted, Formation of, 319
 - Pasted, Preparation of, 299
 - Platté formed, Preparation of, 301
 - Porosity of, 256
 - Position of Support Relatively to, 274
 - Preparing, Methods of, 16, 297
 - Properties of, 256
 - Quick-formed, Preparation of, 301
 - Relative Weight and Volume of, 266
 - Resistance of, 225, 258
 - Specific Output of, 260, 268
 - Strength of, 259
 - Thickness of, 261
- Alkaline Cells**, 128, 133
- Antimonious Lead**, Use of, in Supports, 291
- Armstrong (H. E.) and Robertson (G. H.)**
on Persulphuric Acid, 209
- Arsenic**, Tests for, 351
- Automatic Cut-in-and-out Switches**, 374
 - Regulation, 383
 - Regulator Switches, 393
- Automobile Cells**, Design of, 284
- Ayrton's (W. E.) Researches**, 151, 152, 179, 190, 198, 207, 248
- Batteries**, Connecting up, 378
 - Erection of, 357
 - First Charge of, 366
- Batteries**, Insulation of, 336, 360
 - Regulating the E.M.F. of, 379
 - Series or High-Tension, 110
 - Stands for, 357
 - Traction, 192, 384
- Booster**, Differential, 388
 - Highfield's, 390
 - Regulation by, 379
- Capacity**, Absolute, 175
 - and Output, Relationship between, 177
 - Practical, Definition of, 177
- Cells**, Alkaline, 128
 - Automobile, Design of, 284
 - Cleaning, 339
 - Chemistry of Lead, 145, 165, 203
 - Connecting up, 362
 - Connectors for, 363
 - Copper/Lead Peroxide, 116
 - Counter E.M.F., 382
 - Depreciation of, 254, 288
 - Design of, 253
 - Erection of, 357
 - Maintenance of, 288
 - Primary, in Relation to Secondary Cells, 5
 - Regulation of, 379
 - Regulator or Reserve, 380
 - Testing of, 346
 - Thermo-chemistry of Lead, 236
 - Temperature Changes in, 248, 250
 - Treatment of, 325
 - Zinc/Copper Oxide, 128, 134
 - Zinc/Lead Peroxide, 118
- Cell-testers**, 372

Charge at Constant P.D., 180, 333
 Characteristic Curves of, 172
 E.M.F. of, 166
 First, 366
 Graduated Rates of, 333
 Polarisation E.M.F.s of, 168
 Polarisation on, 166
 Reactions of, 165, 228
 Temperature Changes during, 248

Chemical Theory, History of, 203

Chemical Testing, 348

Cleaning Cells, 339

Connecting-up Batteries, 378

Cells, 362

Connectors for Cells, 363

Constant P.D., Charging at, 180

Cooling of Cells on Discharge 250

Copper in Lead, 294

Tests for, 350

Crawley's Automatic Cut-in-and-out, 377

Darrieus' Views on Discharge Reactions, 210

Definitions, 6

Depreciation of Cells, 254, 288

Design of Cells, 253

Diffusion in Relation to Discharge P.D., 163

Discharge, Characteristic Curves of, 153

Double Sulphation Theory of, 146, 205, 209, 215

E.M.F. of, 147, 149, 243

Oxidisation Theory of, 211

P.D. of, 150, 152, 153, 162, 184

Polymerisation Theory of, 220

Reactions of, 145, 226

Temperature Changes during, 248

Double Sulphation Theory of Discharge, 146, 205, 209, 215

Drake (B. M.) and Gorham (J. M.) on Local Action, 206

Duncan (L.) and Wiegand (H.), Researches of, 207, 208, 250

Earle's (H. A.) Researches, 169

Efficiency, Causes of Variations of, 191

Definition of, 189

Determination of, 190

Hopkinson's (B.), Researches on, 193

Of Traction Batteries, 192

Electrodes, Arrangement of, 103

Characteristics of, 9

Classification of, 9

Components of, 8

Design of, 274

Double Grid or Lattice, 28, 277

Formed, 9, 83

Electrodes, Faure Type, 9, 19

Grid, 19, 275

Grooved, 35, 83, 275

Metallic Envelope, 73, 275, 276

Moulded Pellet, 43

Output for Weight and Volume of, 269

Pasted, 9, 19

Planté Type, 9, 83

Plugged, 11, 77

Porous, 100

Position of, 282

Protected, 46, 283, 289

Ratio between Active Material and Support in, 271

Recessed and Pocket, 35

Relations between Positive and Negative, 272

Ribbed, 35, 83, 275

Rod, 59

Separating, 282

Sheet, 64, 88, 275

Strip, 64, 92

Studded, 38

Supporting, 283

Support Surface of, 265

Trough and Bar, 38

Tubular, 59

Volckmar type, 11, 77

Wire, 71

without Supports, 9

Electrolyte, Calculation of Quantity of, 280

Effect of Sodium Sulphate in, 337

E.M.F. in Relation to Strength of, 149

Impurities in, 324, 348

Management of, 344

Strength of, 277

E.M.F., Charge, 166

Discharge, 149, 243

Relations between Strength of Electrolyte and, 149, 208

Thermo-chemical Calculation of, 146, 236

Erection of Cells, 357

Evershed and Vignoles' Cell Tester, 373

Faure type Electrodes, Characteristics of, 9, 19

FitzGerald's (D.) Theories of Discharge, 209

Formation, Cost of, 307

Efficiency of, 308

of Pasted Active Material, 319

Planté, 299

Quality of, 309

Quick, 301

Reliability of, 312

Solutions for, 303

Formed Electrodes, Characteristics of, 9

Frankland's (E.) Researches, 205, 207

- Gas Battery, Grove's, 2
 Gladstone and Hibbert's Researches, 184, 208
 Gladstone and Tribe's Researches, 204, 206, 209
Grid Supports, 19, 28, 275
 Moulds for Casting, 296
 Grooved Supports, 35, 83, 275
 Grove's Gas Battery, 2
- Heats of Dilution of Sulphuric Acid, 245
 Heats of Formation, 239
 Heim's Researches, 184
 "Highfield" Booster, 390
Highfield (J. S.), on Battery Efficiency, 193
 on Booster Regulation, 383, 385
 "High-tension" Batteries, 110
 Hopkinson's (B.) Researches, 193
 Hurst's Hydrometer, 372
 Hydrochloric Acid, Tests for, 354
 Hydrometers 369
- Impurities in the Electrolyte**, 234, 324, 348
 in Lead, 292
 left over from Formation, 311
 Internal Resistance, 197
 Insulators, Oil, 360
 Iron, Tests for, 349
- Joule's Equivalent applied to Calculations of E.M.F., 236
- Keating's Hydrometer, 370
- Lead Chloride as Raw Active Material, 323
 Lead Compounds, Characteristics of, 220
 Lead Oxide (Litharge), 299, 313
 Lead Oxide (Minium or Red Lead), 221, 223, 299, 314
 Lead Oxides in Presence of Free Acid, Behaviour of, 213
 Lead Peroxide, 215, 258, 346
 Lead, Purity of, 292
 Liagre's Researches, 185
Local Action at Positives, Nature of, 206
 in Cells, 234
 Lodge (O.) on Theories of Discharge, 204
- Maintenance of Cells, 254, 288
 Manganese, Tests for, 350
 Minium, 221, 223, 299, 314
- Nalder Bros. and Thompson's Cell Tester, 373
 "Neville" Automatic Cut-in-and-out, 376
 Nickel Oxides, Characteristics of, 143
- Nitric and Nitrous Acids in Quick Formations**, 304
 Tests for, 353
 Nomenclature, 6
- Occluded Gas Theory of Discharge, 203
Overcharging, 332
 Output and Capacity, Relations between, 177
Output, Ayrton's Researches on, 179
 Causes of Variation of, 178, 262
 in Relation to Support Surface, 265
 per Unit Weight and Volume of C-II, 284
 Relative, of Positives and Negatives, 272
 Weight Relatively to, Reynier upon, 287
- Pasted Active Material, Preparation of, 513
 Pasted Electrodes, Characteristics of 9, 19
 Pasting, 314
P.D., Charge, Curves of, 172
 Charging at Constant P.D., 180, 333
 Discharge, 150, 152, 153, 162, 184
 Peroxide of Lead, 215, 258, 346
 Persulphuric Acid, 168, 209
 Planté's Researches, 3, 203
 Planté type Electrodes, Characteristics of, 9, 83
 Plugged Electrodes, Characteristics of, 11
Polarisation, Early Views of, 2
 or Charge, 166
 Polarity of Secondary Cells, Definition of, 7
 Polymerisation Theory of Discharge, 220
 Preece (W.) on Internal Resistance, 198
 Primary Cells in Relation to Secondary Cells, 5
 Protected Electrodes, 46, 283, 289
- Recessed and Pocket Electrodes, 35
 Records of Treatment, 343
 Red Lead, 221, 223, 299, 314
Regulating Switches, 380
 Automatic, 393
Regulation, Automatic, 383
 by Boosters, 383
 by Counter E.M.F. Cells, 382
 by Reserve Cells, 380
 of Traction Batteries, 384
 Regulator or Reserve Cells, 342, 380
 Reversal, Reactions of, 227
 Reynier (E.) on Output and Weight of Cells, 287
 Ribbed Electrodes, 35, 83, 275
 Robertson (G. H.) on Persulphuric Acid, 209

- Rod Electrodes, 59
 "Rooper" Cell Connector, 364
- Seasoning Pasted Active Material, 318
 "Series" Batteries, 110
 Sheet Electrodes, 64, 88, 275
 Sodium Sulphate in Electrolyte, 337
 Specific Gravities of Dilute Sulphuric Acid, 278, 367
 Specific Resistances of Dilute Sulphuric Acid, 161
 Strength of Acid in Relation to E.M.F., 149, 208
 Strip Electrodes, 64, 92
 Studded Electrodes, 38
 Sulphation, Abnormal, 148, 233, 325, 336
 Sulphuric Acid, Heat of Dilution of, 245
 Impurities in, 324
 Specific Gravities of Dilute, 278, 367
 Specific Resistances of Dilute, 161
- Supports, Casting, 295
 Conductivity of, 262, 291
 Definition of, 9
 Design of, 274
 Double Grid or Lattice, 28, 277
 Grid, 19, 275
 Grooved, 35, 83, 275
 Material of, 14, 291
 Metallic Envelope, 73, 275, 276
 Nominal and Actual Surface of, 264
 Output in Relation to Surface of, 265
 Ratio between Active Material and, 271
 Recessed and Pocket, 35
 Resistance of, 262, 291
 Ribbed, 35, 83, 275
 Rod, 59
 Sheet, 64, 88, 275
 Strip, 64, 92
 Studded, 38
 Surface per Unit Weight of, 264
 Thickness of, 263, 271
 Treatment before Pasting, 297
- Supports, Trough and Bar, 38
 Tubular, 59
 Volume of Active Material Relatively to Surface of, 267
 Wire, 71
- Swinburne (J.) on Variation of E.M.F., 208
- Switches, Automatic, 374, 393
 Regulating, 380, 393
- Temperature and Output, Relations between, 182
- Temperature Changes during Charge and Discharge, 248
- Testing, Chemical, 348
 Commercial, 342
 Laboratory, 346
- Tests for Arsenic, 351
 Copper, 350
 Hydrochloric Acid, 354
 Iron, 349
 Manganese, 351
 Nitric and Nitrous Acids, 353
- Thermo-chemical Calculation of E.M.F., 236
- Thomson's Law, E.M.F. According to, 236
- Traction Batteries, 192, 384
- Treatment of Short-Circuited Cells, 339
 of Sulphated Cells, 336
 on Discharge, 326
 on Open Circuit, 334
 on Recharge, 338
 Records of, 342
- Trough and Bar Electrodes, 38
- Tubular Electrodes, 59
- Volckmar Type Electrodes, 11, 77
- Voltmeters, Cell-testing, 372
- Wade's (E. J.) Theories of Discharge, 210
- Wire Electrodes, 71
- Zinc/Copper Oxide Cells, 128
- Zinc/Lead Peroxide Cells, 118

INDEX

TO

NAMES OF CELLS AND ELECTRODES.

(CHAPTERS II., III. AND X.)

- "A. B. P.," 423
 Accumulator Industries, 427
 "A. F. A. G.," 85, 410, 451
 Akester, W. H., 93
 "Allan," 433
 American Battery Co., 99, 445
 Andreoli, E., 18, 32
 Andrews, M. M., 64
 "Armoured," 434
 Arnould, E., 100
 Aron, H., 133
 Ashmore, Benson, Pease & Co., 423
 Askew, C. B., 50
 "Atlas," 108
- Bailey, M., 72
 Bailhache, G., 129
 Bailly, P., 102, 119
 Barber-Starkey, W. J. S., 62
 Barbier, C. J., 76
 Barrier, J. J., 93
 Beaumont, W. W., 44, 71, 89, 100, 101
 Beeman, J. S., 93, 97
 "Behrend," 461
 Benardos, N. de 96
 Benjamin, P., 119
 Berks, R. R., 88
 Borliner Co., 455
 Beyer, C., 32
 "B. G. S.," 471
 Biggs, C. H. W., 71, 89, 100, 101
 "Bleistaub," 454
 "Blot," 467
 "Blot-Fulmen," 467
 Blot. G. R., 99
 Bot tcher, K. E., 118
- "Boose," 457
 Bouquet, Garcin and Schivre, 471
 Bousignac, L. de, 129
 Boys, C. V., 101
 British Power, Traction and Lighting Co., 426
 Brophy, J. D., 64
 Brush, C. F., 14, 19, 20, 35, 38, 64, 71, 83, 84, 90
 "B. T. K.," 97
 Buckland, W. A. B., 55
 Burns, J., 110
- Cameron, H. F., 25
 Carpenter, H. H., 74
 Carpentier, J., 95, 118
 Cathcart, C. H., 118
 Chaperon, G., 128
 Cheswright, H. T., 68, 87
 "Cheval-Lindeman," 479
 Chloride Electrical Storage Syndicate, 406
 "Chloride," American, 439
 "Chloride," English, 406
 "Chloride," French, 462
 "Clare," 446
 Clark, E., 26, 34
 Colgate, A. E., 99
 "Commelin and Vian," 124, 482
 Commelin, E., 129
 "Conrad," 450
 Cookson, N. C., 101
 "Correns," 460
 Correns, E., 31
 "Crompton-Howell," 103, 400
 Crompton, R. E., 100
 Crowds, W. A., 69

- Currie, C., 60
 Cuttriss, T., 100
- D'Arsonval, A., 118
 "D'Arsonval-Vaugeois," 468
 De Benardos, N., 96
 "De Dion-Bouton," 480
 De Kabath, N., 71, 74, 78, 88, 94
 De Lelande, F., 128
 De Meritens, A., 90
 Desmazures, C., 129
 "Dinin," 435
 Dolter, H., 113
 Donaldson, W. W., 76
 Dorman, G. E., 94
 Doubleday, V. C., 55, 68
 "D. P.," 401, 431
 Drake, B. M., 23
 Dujardin, P. J. R., 17, 96, 124
 Dun, A., 133
 Durham, F. W., 71
- Eaton, A. K., 71
 Edgerton, N. H., 112
 Edison, T. A., 137, 480
 Eickemeier, R., 107
 Electrical Power Storage Co., 22, 26, 59, 395
 Electric Storage Battery Co., 52, 82, 439
 Elieson, C. P., 79, 89, 106
 Elwell, P. B., 17
 Emmens, S. H., 96
 Entz, J. B., 72, 130
 "E. P. S.," 22, 26, 59, 395
 "Epstein," 403
 Epstein, L., 17, 39, 43, 74, 101, 123
 Ernst, V. H., 107
 Ewing, T., 66
 "Exide," 441
- Farbarky, S., 28
 Faure, C. A., 4, 19, 47, 56, 71, 73, 103, 111, 112, 113, 114, 298
 "Faure-King," 56, 399
 FitzGerald, D. G., 14, 15, 16, 19, 49, 1, 89, 100, 101
 Foote, T. M., 39
 Frankland, E., 19, 44
 "F. S. V.," 20, 25
 "Fulmen," 470
- Gadot, D. L. M., 25
 Gardner, E. M., 64
 Geoffroy and Delore, 417
 Gérard-Lescuyer, J. M., 18
 Germain, P., 25
 Gibson, C. D. P., 23, 29, 67, 80, 107
 Giovanni, G., 35
- Glaesener, 97
 Gorham, J. M., 23
 "Gould," 441
 Grindle, R. J. W., 83
 Griscom, W. W., 80
 Groszwith, H., 76
 Grout, G., 101
 Guelzow, L., 69
 "Gulcher," 435
 Gulcher, R. J., 73
- "Hagen," 451
 Hagen, G., 32
 Hall, C. J., 81
 Harris, G. W., 87
 Harris, T., 25
 "Hart," 419
 Hartung, M., 22
 Hasslacher, F., 134
 Hatch, 52, 447
 Hathaway, J. G., 438
 Hauser, H., 41
 Headland, H. W., 42
 Heilmann, J. J., 479
 "Heinz," 471
 Hering, C., 108
 "Hess," 50, 55
 Heyl, G. E., 28, 87, 102
 Hochausen, 84
 Hofmann, J. E., 35
 Holden, H. C., 40
 Holdrege, S. L., 75
 Holland, R. J., 87
 Houston, 115
 Howard, G., 60
 Howell, J. C., 102
 Humphrey, 29
- "Ideal," 438
 "I. E. S.," 56
 International Storage Battery Co., 446
 "Invicta," 423
- Jahr, R. H., 35
 Jarman, J., 15
 Jaquet, M., 25
 Joel, H. F., 101, 102, 438
 Johnson, G. A., 75
 Jones, E., 93
 Jones, T. J., 14, 70
 Jones, W. H., 101
 Julien, E., 15, 110, 114, 124
- Kabath, N. de, 71, 74, 78, 88, 94
 Kalischer, S., 15
 "K. A. W.," 451
 Kennedy, C. W., 76

- Kennedy, R., 111
 Kennedy, P., 70
 "Khotinsky," 454
 Khotinsky, A. de, 36, 71, 106
 King, F., 26, 34, 56, 97
 Kingzett, C. T., 15
 Knowles, E. R., 61, 74
 Kookogey, W. P., 70

 "Lalande-Chaperon," 128
 "Lamina," 106
 Lane-Fox, St. G., 93
 Laurent-Cély, A. M. F., 18, 25, 45
 Lea, J., 15
 Lee, C. E., 124
 Lee, J. B., 62
 "Leecoll," 481
 Legay, K. and L., 72
 Lehmann, A., 35, 417, 456
 "Leitner," 427
 Leitner, H., 123
 "Lithanode," 430
 Lloyd, H. H., 50
 Lodge, O., 119
 Logan, C. H., 37, 75
 Longstreth's, Ltd., 430
 Lyte, F. M., 15, 17, 25, 43, 70

 Macrae, R., 76
 Main, W., 89, 120
 "Majert," 473
 "Manchester," 82
 March, O., 68
 Marchenay, A., 18
 "Marquand," 435
 Marquand, A. J., 103
 "Max," 478
 McDougall, W. M., 69
 Menges, C. L., 22, 54
 Meserole, A. V., 120
 Michalowsky, T. de, 134
 Monnier, D., 100
 "Monobloc," 431
 Montaud, C. B., 18
 Morrison, W., 97
 Mower, H., 67
 Muirhead, A., 18
 Müller, A., 86
 "Mulden," 456

 "National," 438
 National Battery Co., 448
 New and Lucas, 482
 Niblett, J. T., 68.

 Oblasser, A., 55
 Oerlikon Co., 20

 "Omega," 417
 Oppermann, C., 438
 "Osburn," 449

 Page, N., 96
 "P and G," 417
 P. and R. Storage Battery Co., 433
 Parker, T., 17
 Payen, C., 18
 Peral, J., 23
 Peto and Radford, 434
 Peyrussan, A. E., 124
 Pezzier, O., 95
 "Phoenix," 476
 Philippart, G., 114, 476
 Phillips, W. A., 72, 130
 Pitkin, J., 38, 40, 49, 101
 Planté, G., 3, 16, 18, 47, 88, 103
 "Pollak," 436, 452
 Pollak, C., 38, 100
 "Pope," 437
 "Porter," 445
 Price, A. P., 49
 Pritchetts and Gold, 417
 "P. T. L.," 426
 Pumpelly, J. K., 50, 106

 Reckenzaun, A., 44
 Renger, J., 88
 "Reuterdahl," 447
 Reynier, E., 90, 101, 117, 119
 Rhodin, J. G. A., 82
 Ribbe, P., 113
 Roe, G. H., 54
 Rooney, J. J., 71
 Rooper & Co., 404
 Rosenthal, S. A., 55, 68, 438

 Schafer and Heinemann, 461
 Schanschieff, A., 68, 111
 Schenck, S., 28
 Schneider, F. W., 35, 42
 Schöller, 35
 Schoop, P., 133
 "Schulz," 461
 Schulz, O., 17, 103
 Sellon, J. S., 14, 15, 20, 22, 30, 38, 39, 49,
 64, 70, 73, 109, 114
 "Sherrin," 437
 Siemens, W., 15
 Simmen, 74, 101
 Smith, C., 79
 Société l'Electrique, 417
 Société pour le Travail Electrique des
 Metaux, 462
 Somzée, 71, 73, 74
 Sorley, C., 65, 85

- "Sperry," 448
 Starr, E. T., 19, 38, 71, 73
 Stetson, A., 74
 "Still," 438
 "Stockton," 423
 Sussmann, M., 68
 Sutherland and Marcuson, 439
 Sutton, H., 15, 116
 Sutro, G., 54
 Swan, J. W., 15, 17, 19, 35, 84
 Swinburne, J. 15

 "Taipo," 438
 Tamine, R., 19, 100, 119
 Tasker, W. H., 14, 70
 Taylor, W., 65, 97
 "T. E. M.," 462
 Thame, H., 63
 Théryc, C., 55, 60
 Thompson, C. H., 100
 Thomson, E., 115
 "Thomson-Houston," 115
 Timmis, I. A., 46
 Tommasi, D., 55, 60, 77, 92, 100
 Tribe, A., 19, 49, 92
 "Tribelhorn," 461
 Tribelhorn, A., 114
 "Tudor," 410, 451
 Tudor, H. O., 16, 23, 36, 85

 "Umpire," 439
 "Union," 473
 Usher, E. P., 53, 67

 Van Gestel, J. T., 37, 40
 Van Raden & Co., 435
 Vaughan-Sherrin, J., 63
 Vaughton, E. R., 50
 Vernède, F. T., 93
 "Victoria," 426
 Virloy, A. de, 129
 Volckmar, E., 11, 20, 73, 77

 Walter, J. H., 81
 Ward, P., 71
 Warner, J., 72
 "Waddell-Entz," 130
 Washburn, G. H., 54, 105
 "Watt," 461
 Watt, A., 100, 101
 "Wehrlin," 461
 "Willard," 444
 Williams, F. T., 102
 Winch, G. L., 49
 Winkler, C. F., 41
 Wladimiroff, N., 111
 Woodward, H., 59, 64
 Woodley, R. H., 101
 "Woven Glass," 435

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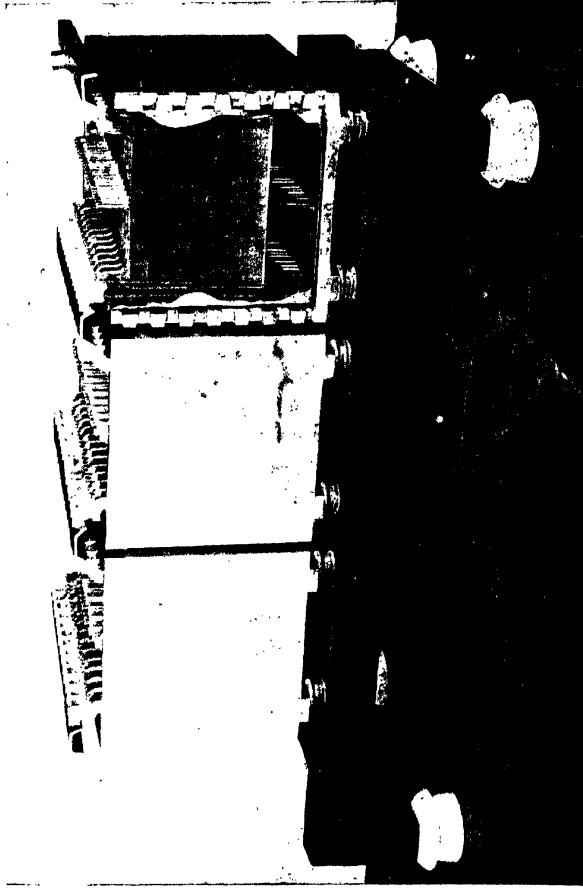
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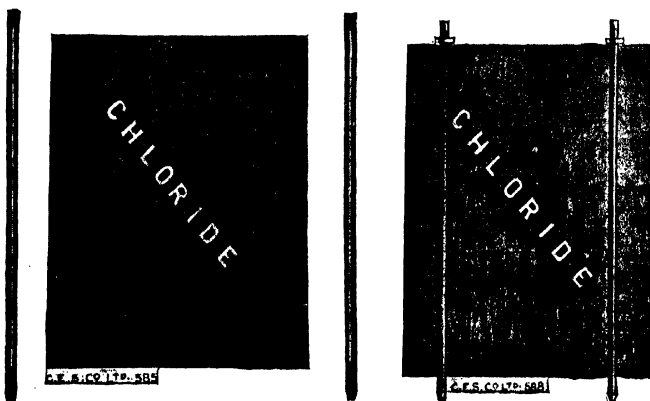
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| " II.—Historical Notes.                                          | X.—Gas Analysis.                                            |
| " III.—Facts concerning Carbon.                                  | XI.—On the Capital necessary for starting Carbon Works, &c. |
| " IV.—The Modern Process of Manufacturing Carbons.               | XII.—The Manufacture of Electrodes on a Small Scale.        |
| " V.—Hints to Carbon Manufacturers and Electric Light Engineers. | XIII.—Building a Carbon Factory.                            |
| " VI.—A "New" Raw Material.                                      | XIV.—Soot or Lamp Black.                                    |
| " VII.—Gas Generators.                                           | XV.—Soot Factories.                                         |
| " VIII.—The Furnace.                                             |                                                             |

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| „ II.—Measurements of Current, Potential, and Battery Resistance. | „ VIII.—Localisation of Disconnections.                               |
| „ III.—Natural and Fault Current.                                 | „ IX.—Localisation of Earth and Contacts.                             |
| „ IV.—Measurement of Conductor Resistance.                        | „ X.—Corrections of Localisation Tests.                               |
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